THE CONSTRUCTION AND TESTING OF A HIGH TEMPERATURE ADIABATIC CALORIMETER

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THE CONSTRUCTION AND TESTING OF A HIGH TEMPERATURE ADIABATIC CALORIMETER

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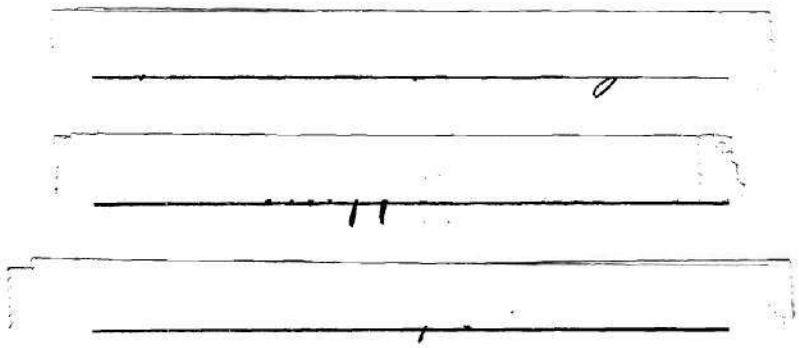

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CHAPTER I

INTRODUCTION

"The addition of heat to a substance frequently results in a temperature rise whose magnitude depends on the mass and on a specific property of the substance".[1]

The following equation is a statement, in differential form, of the above quotation:

$$dq = mc\,dt$$

dq = infinitesimal quantity of heat added
m = mass of the substance
dt = infinitesimal temperature rise
c = a constant

The constant, c, is defined by this expression and is called the "specific heat". The product, mc, has been termed "heat capacity" but usage of the two terms is interchangeable and will be so used in this paper.

The constant, c, depends on the manner in which heating

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(1) B. F. Dodge, Chemical Engineering Thermodynamics, McGraw-Hill Book Co., Inc., (1944), p. 25.

takes place and is characteristic of the substance involved. Two useful concepts of c are C_p, the heat capacity at constant pressure, and C_v, the heat capacity at constant volume.

We may then state: at constant pressure,

$$dq = m\, C_p\, dt$$

In a similar manner, a mean specific heat at constant pressure, $\overline{C}_p$, may be defined by:

$$\overline{C}_p = \frac{q}{m\ (t_2 - t_1)}$$

for a finite quantity of heat added which causes a finite temperature rise.

Inspection of this equation shows that a weighed sample, to which a measured quantity of heat is added and the temperature rise measured, provides a means of determining the value of the mean specific heat at constant pressure. If the temperature rise is small, then we have approached the value of an instantaneous specific heat.

Specific heat data are a very important tool in many thermodynamic calculations. The thermodynamic functions of entropy, enthalpy, and free energy can readily be expressed as functions of temperature with accurate specific heat data. Calculation of heats of reaction, free energy changes, and various relations between thermodynamic functions are some of the uses of these data.

The purpose of this paper is to describe the construction and testing of an apparatus for determining values of the

mean specific heat at constant pressure of solids and liquids over small temperature ranges between 0°C and 150°C.

The sample of solid or liquid may be weighed very accurately and the change in temperature may also be measured with a comparable accuracy by use of a resistance thermometer or thermocouple. However, the measurement of the exact quantity of heat added to a substance is much more difficult. It is extremely difficult to prevent the escape of heat from a body and the degree of accuracy attainable in calorimetric measurements is largely dependent on minimizing this loss of heat and estimating those losses that cannot be eliminated. Probably for this reason, the control of heat losses determines the various names applied to calorimeters; e. g., ice, Joule's twin-type, vacuum-walled, convection shield, aneroid, adiabatic, et cetera.

The adiabatic type functions on a prinicple of the Second Law of Thermodynamics; viz., there will be no net change of heat between two bodies at the same temperature. The sample is surrounded by a shield, electrically heated or otherwise susceptible to temperature control, which is maintained at the temperature of the sample.

The adiabatic calorimeter which will be described can be used to determine specific heats and heats of transition of solids and liquids in the temperature range from 0°C to 150°C. The absolute accuracy of specific heat

measurements as determined in the range above room temperature was 3%. Some modifications can improve this accuracy to better than 1%. Inaccuracies due to heat losses have been minimized and at present constitute only about one-tenth of the total error.

CHAPTER II

GENERAL DISCUSSION OF THE ADIABATIC TYPE CALORIMETER

White[2] reported that the first use of the adiabatic method was by Person in 1849. Considerable work on this method was done by T. W. Richards following 1909.[2] His work appears to have brought the adiabatic method to the fore and many investigators began using variations of the original.

The introduction of the adiabatic method allowed larger air gaps (between calorimeter and shield) to be employed safely and thus lessened the errors due to thermal leakage.

The control of the temperature of the adiabatic shield was done in various ways. Neutralization of alkali by acid allowed an easy method of heating. The rate of heating could easily be determined and controlled.

Another obvious method was the use of hot water in the adiabatic jacket. In this method some automatic control of the hot water flow by the calorimeter temperature was used.

Electric heating of the jacket or shield has been used extensively. It is particularly convenient and allows complete enclosing of the calorimeter can. Other methods encountered

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(2) Walter P. White, The Modern Calorimeter, The Chemical Catalog Co., Inc., (1928), p116ff.

difficulties in producing liquid seals particularly for the top. The liquid had to be stirred in order to maintain a uniform temperature, and the liquid chamber had to be available for stirring mechanisms.

Further minimizing of heat losses due to convection was obtained by evacuating the air gap between calorimeter can and adiabatic shield. Use of electric heaters throughout and thermocouples for temperature measurement makes it possible to completely and easily seal off the entire apparatus, and permits the maintenance of a high vacuum space which completely surrounds the calorimeter can.

Southard and Andrews[3] constructed an adiabatic calorimeter for use at low temperature. A calorimeter can made of gold-plated copper was suspended inside an adiabatic shield and the shield and calorimeter can placed in a large glass tube which was connected to a vacuum system. A dewar vessel filled with liquid air surrounded this assembly.

The calorimeter can was heated by an internal latticework of platinum-iridium wire and temperature changes were measured using a copper-constantan thermocouple mounted on the outside of the can.

The shield was a copper cylinder, heated by a constantan heater. Automatic control was used on this heater by a sensitive mirror galvanometer which operated a photo-electric-cell-

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(3) John C. Southard and Donald H. Andrews, J. Franklin Inst., 209, 349, (1930)

relay device. A copper-constantan difference thermocouple between the can and shield actuated the galvanometer.

Results consistent to about 1/2 percent were obtained in measurements on toluene and benzene.

Southard and Brickwedde[4] used a vacuum calorimeter with an electrically heated shield to determine the heat capacity of naphthalene from 14° to 300° K. A thermal shield heated by three separate electrical heaters completely enclosed the calorimeter can. An outer jacket enclosed the entire apparatus. The space between the inner calorimeter can and the outer jacket was connected to a high vacuum system. A refrigerating bath of liquid air or liquid hydrogen was used to maintain low temperatures. This type of calorimeter performed very satisfactorily and was especially good in measurements of slow thermal transitions since a constant, small thermal head could be maintained between the inner can and adiabatic shield.

In June, 1946, Dr. W. T. Ziegler of the Georgia Tech Engineering Experiment Station completed the design of the adiabatic calorimeter presently to be described. He incorporated the most desirable features of the aforementioned calorimeter types, and added some new features. The electrically heated adiabatic shield is used and an additional

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(4) John C. Southard and F. G. Brickwedde, J. Am. Chem. Soc., 55, 4378, (1933)

"stabilizer" shield protects the adiabatic shield from heat loss and makes for more ease in maintaining zero temperature differences around the inner calorimeter can. None of the preceding calorimeters were used above 25°C. The present design is intended for use up to 150°C.

More recently Stow and Elliot[5] have described an adiabatic calorimeter before the 111th meeting of the American Chemical Society at Atlantic City, New Jersey. Their instrument consists of a sterling silver can suspended inside a silver adiabatic shield which is in turn suspended in a brass can. The entire assembly is placed in an oil bath and evacuated. A platinum resistance thermometer-heater was placed inside the calorimeter can and the temperature determined by use of a Mueller bridge. A photo-electric-cell-relay device in conjunction with a galvanometer and a pair of difference thermocouples controlled the temperature of the adiabatic shield. Heat capacities with a precision of ±5 percent in the range of 50°C to 250°C were determined.

It is well to point out here that these two designs were made independently and are apparently the first attempts to utilize this type of calorimeter at temperature above 25°C.

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(5) Frederic S. Stow, Jr., and J. H. Elliott, Analytical Chemistry, Vol.20, No. 3, 250, (1948)

CHAPTER III

CONSTRUCTION

The calorimeter and accessory parts will be considered as three systems for purposes of clarification in discussing their construction. These systems will be: calorimeter assembly, vacuum system, and electrical control systems. This chapter will deal only with the calorimeter assembly and vacuum system. The controls will be discussed in a later chapter.

The calorimeter assembly consists of the calorimeter can, the copper adiabatic shield, the aluminum stabilizer shield, the outer can and insulated box, and their integral parts. Figure I shows the general details of the calorimeter assembly. Appendix A, Figure 10, is a photograph of the various parts. The cans and shields are all closed cylinders. The calorimeter can is surrounded by the copper adiabatic shield, these two being in turn surrounded by the aluminum stabilizer shield, and all three are then surrounded by the outer can. This entire assembly is then placed in an insulated box.

The calorimeter can, L, which contains the sample, is made of copper and the entire surface was gold plated by the Southern Electro Plating Co., 15 Elliott St., S. W., Atlanta, Ga. It is cylindrical with a removable top. The dimensions are: 1 1/8" diameter, 2 1/8" long, and 0.032" wall thickness.

LEGEND FOR FIGURE I

A. 3/4" diameter Inconel tube to Vacuum System

B. Monel Ferrule

C. Outer can (Vacuum Jacket)
   4" Seamless Brass tube
   0.040" wall, 8" long

E. Stabilizer Shield
   3" Aluminum tube - 6" long and 0.065" wall
   Inside surface has bright finish

F. Suspension Wires

G. Thermocouple Wires

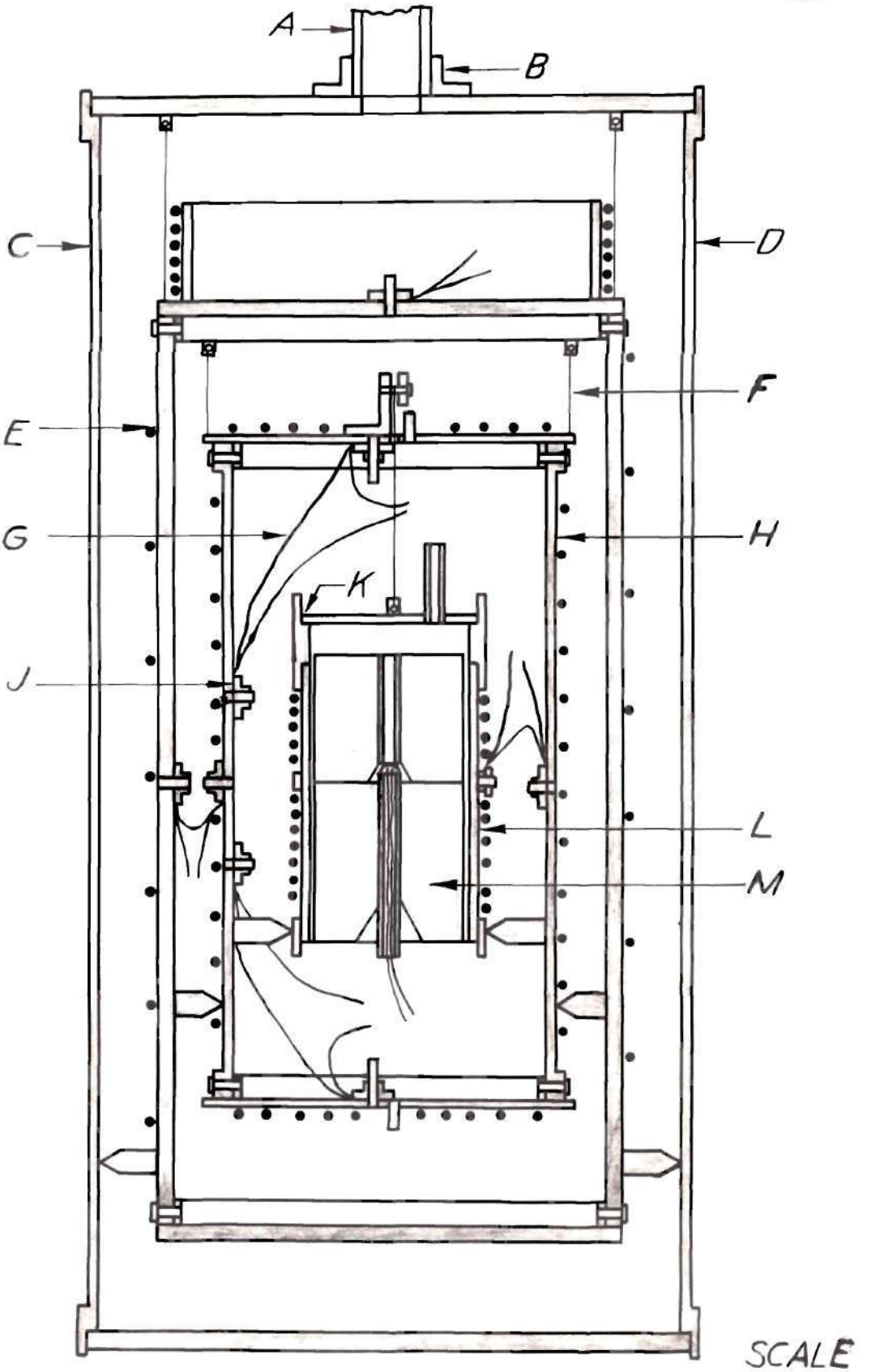
H. Adiabatic Shield
   2 1/8" Copper tube - 4 3/16" long and 0.040" wall
   Inside surface has morror finish

J. Thermocouple junction

K. Pure Tin Soldered Joint

L. Calorimeter Can

M. Copper vanes - 0.010" thick



ADIABATIC CALORIMETER

FIG 1

The volume of the can is approximately 24 ml. It was fabricated and then vacuum tested for leaks. No leaks were detected.

Inside the can are copper fins, M, in two sections which aid in heat transfer and in the maintenance of a uniform temperature throughout the sample which is placed here. The top section is removable and the bottom is brazed with Harmon and Handy Easy-Flo brazing alloy to the thermocouple well inside the can. There are 8 fins which radiate outward from the center. They measure 0.010" thick with a micrometer.

The top can be removed to insert or remove the sample and is soldered on vacuum tight with a pure tin solder joint, K, to a monel metal insert on the calorimeter can. Pure tin solder is used to permit temperatures up to 200°C. The top is fitted with a small tube that may be used to fill the can with helium gas which furnishes an inert atmosphere and also conducts heat better than air. In the center of the top is a hook to which a #28 B. and S. gage nichrome wire is attached. This wire suspends the calorimeter can from the top of the copper adiabatic shield.

Inside the can a small tube extends upwards from the bottom approximately one-half of the length of the can up through the center. This is the thermocouple well. On the upper end of this tube, inside the can, a copper-constantan thermocouple is soldered with pure tin solder; the leads of the thermocouple go out inside this tube through the bottom of the can.

Around the outside of the can, midway between top and bottom, is a band of exposed metal; i. e., no heating wires are wound here. On this band one junction of a difference thermocouple is attached. This difference thermocouple is between the calorimeter can, L, and the adiabatic shield, H.

A heating coil is wound on the exterior of the calorimeter can. This coil consists of one layer of #32 B. and S. gage D. N. (nylon) enameled constantan wire which is coated with Bakelite lacquer B and baked at 130°C for thirty minutes. There are ninety turns total from which two pairs of leads, #32 B. and S. gage D. S. enameled copper wire, are taken, one pair for current measurements and the other pair for potential measurements. The bottom half of the coil has 57 turns of heating wire and the top half has 33 turns. This coil has a resistance of approximately 125 ohms.

The calorimeter can, less wires but including top and vanes, weighs 60.8 grams.

The adiabatic shield, H, completely surrounds the calorimeter can. This shield is made of copper tubing, with removable top and bottom, and is electrically heated by three constantan heaters, one on each end and on the body. Difference thermocouples between the body and each end, and between the calorimeter can and body of the shield supply the information which is used to control the heaters. The three separate heaters are used to permit some flexibility of control in case non-uniform temperatures result.

The adiabatic shield is a gold-plated copper cylinder. The gold plating is 0.001" thick. The dimensions are 2 1/8" in diameter, 4 3/16" long and has a 0.40" thick wall. The adiabatic shield less wires weighs 218.5 grams. The top weighs 31 grams, the bottom 26 grams, and the body 161.5 grams. The top and bottom may be removed by removing small screws which hold them in place. At the bottom of the shield are two slots in the side to permit passage of thermocouple and heating wires. At the top is another slot in the side for the same purpose.

The inside surface of the shield has been polished to a mirror finish. This was done to reduce heat transfer by radiation. The outside surfaces of both calorimeter can and adiabatic shield were also polished but the installation of the heating coils has made the finish something less than that of a highly polished gold surface.

Three spacers of bakelite composition keep the calorimeter can centered radially inside the adiabatic shield. As shown in Figure I, these spacers have a pointed end and in contact with the calorimeter can.

The heating coils on the exterior of the main body of the adiabatic shield are made of #30 B. and S. gage D. N. enameled constantan wire and has approximately 110 turns in a single layer. The coil is covered with a generous film of Bakelite lacquer B.

The top heater is made of #36 B. and S. gage D. N. enameled constantan wire. It is installed in the approximate form of a flat helical coil and has a resistance of 26 ohms. This coil is lacquered to the exterior of the top with Bakelite lacquer B.

The bottom heater is quite similar to the one on the top. It is made of #36 B. and S. gage D. N. enameled constantan wire and has a total resistance of 20 ohms. The resistances of the heaters are approximately proportional to the masses which they heat. This was done to permit series operation of the heaters if it became desirable to do so.

The constantan wires from every heater are spliced to #32 B. and S. gage D. S. enameled copper leads near the end of each coil. There are three difference thermocouples installed on the copper adiabatic shield. They are made of #32 B. and S. gage D. S. enameled copper wire and #32 B. and S. gage D. N. enameled constantan wire. The junctions are soldered with pure tin solder. One difference thermocouple is installed with a junction on the inside center of the top and inside the body approximately halfway between top and bottom. Another difference thermocouple is similarly installed on the bottom and the body. The third difference thermocouple is placed with one junction on the inside of the adiabatic shield and the other junction on the outside of the calorimeter can,

halfway between top and bottom on each.

The junctions were attached as follows: The metal surface is lacquered with Bakelite lacquer B. Then a small and very thin mica washer was placed on the metal surface from which a small copper pin protrudes. The thermocouple junction was lacquered and dried. The junction was again lacquered, placed on the mica washer and covered with another mica washer. Thus the mica washers were cemented to the junction by fresh lacquer. Then a metal brass washer, the bottom surface of which has been previously lacquered, was held down firmly on the junction as it was soldered to the copper pin with pure tin solder. Care was taken to prevent the thermocouple from coming in contact with any exposed metallic surface. It is necessary to prevent electrical contact between the junctions and the metallic parts of the adiabatic shield because there are several such difference thermocouples and if short circuits developed than the junctions would be connected by a copper conductor, the adiabatic shield body, in addition to the constantan wire and the thermocouple characteristics would be variable and unknown. By using the above method of installation, it is felt that electrical contact is eliminated by the Bakelite B lacquer and the thin mica sheet while reasonably good thermal contact is established.

The adiabatic shield is suspended by three #28 B. and S. gage nichrome wires, F, which are attached to the outer edge of the top of the adiabatic shield and the top of the aluminum stabilizer which surrounds it.

All the thermocouple and heating wires which go to the adiabatic shield and the calorimeter can pass four times around the adiabatic shield and thence to the heaters and thermocouple junctions, respectively. Heat loss by conduction along the wires is minimized in this manner.

The calorimeter can and the copper adiabatic shield are completely surrounded by the aluminum stabilizer shield, E, a closed cylinder of aluminum tubing which is also electrically heated. The dimensions of the shield are: 3" in diameter, 6" long and 0.065" wall.

The top and bottom may be removed by removing small screws which hold them to the main body of the shield. The top has a 3" diameter aluminum ring fitted on it. This ring is 5/8" wide and is electrically heated by a #32 B. and S. gage D. N. enameled constantan wire heater which is wound around the top of the ring. There are two turns of wire whose total resistance is 9 ohms. All the wires going into the calorimeter assembly pass once around the aluminum ring as they enter the calorimeter assembly. The wires are lacquered to the aluminum ring with Bakelite lacquer B. A copper- constantan thermocouple is placed on the top of the aluminum stabilizer shield inside the ring. This thermocouple measures the temperature of the top of the shield and furnishes information for the control of the top heater which is maintained at the temperature of the calorimeter can. The ring serves

as a thermal dam to prevent appreciable heat leak along the wires. Around the edge of the top are three equally spaced holes to which are attached small wires which support the aluminum stabilizer shield from the top of the outer can.

The body of the shield has a heater of #32 B. and S. gage D. N. enameled constantan wire. There are eight turns from top to bottom and the total resistance of the wire is 39 ohms. This heater is held in place with Bakelite lacquer B and baked.

Both heating coils on the aluminum stabilizer shield are connected to #32 B. and S. gage D. S. enameled copper leads.

On the outside of the shield near the bottom are three equally spaced bakelite pins with tapered points which serve to center the aluminum shield radially inside the outer can. On the inside of the shield, and similarly placed, are three like pins which center the copper adiabatic shield in the radial direction inside the aluminum stabilizer shield.

A copper-constantan difference thermocouple which has one junction the outside of the copper adiabatic shield and the other junction on the inside of the aluminum stabilizer shield acts as an indicator for the control of the aluminum shield heater. The temperature of the shield may therefore be maintained at the temperature of the calorimeter can. The thermocouple junctions are attached in the same manner as the difference thermocouple junctions on the copper adiabatic

shield; i.e., electrically insulated from the metal surface but still in relatively good thermal contact.

The bottom of the aluminum shield has no heater. It is easily removable by removing three small screws. When the aluminum stabilizer shield and the bottom of the copper adiabatic shield are removed the calorimeter can may then be dropped down out of the assembly by loosening its wire hanger. The top of the calorimeter can may be unsoldered and the sample changed. The heating and thermocouple wires attached to the calorimeter can and the adiabatic shield bottom are made of sufficient length so that these parts may be removed for this operation without disconnecting any wires.

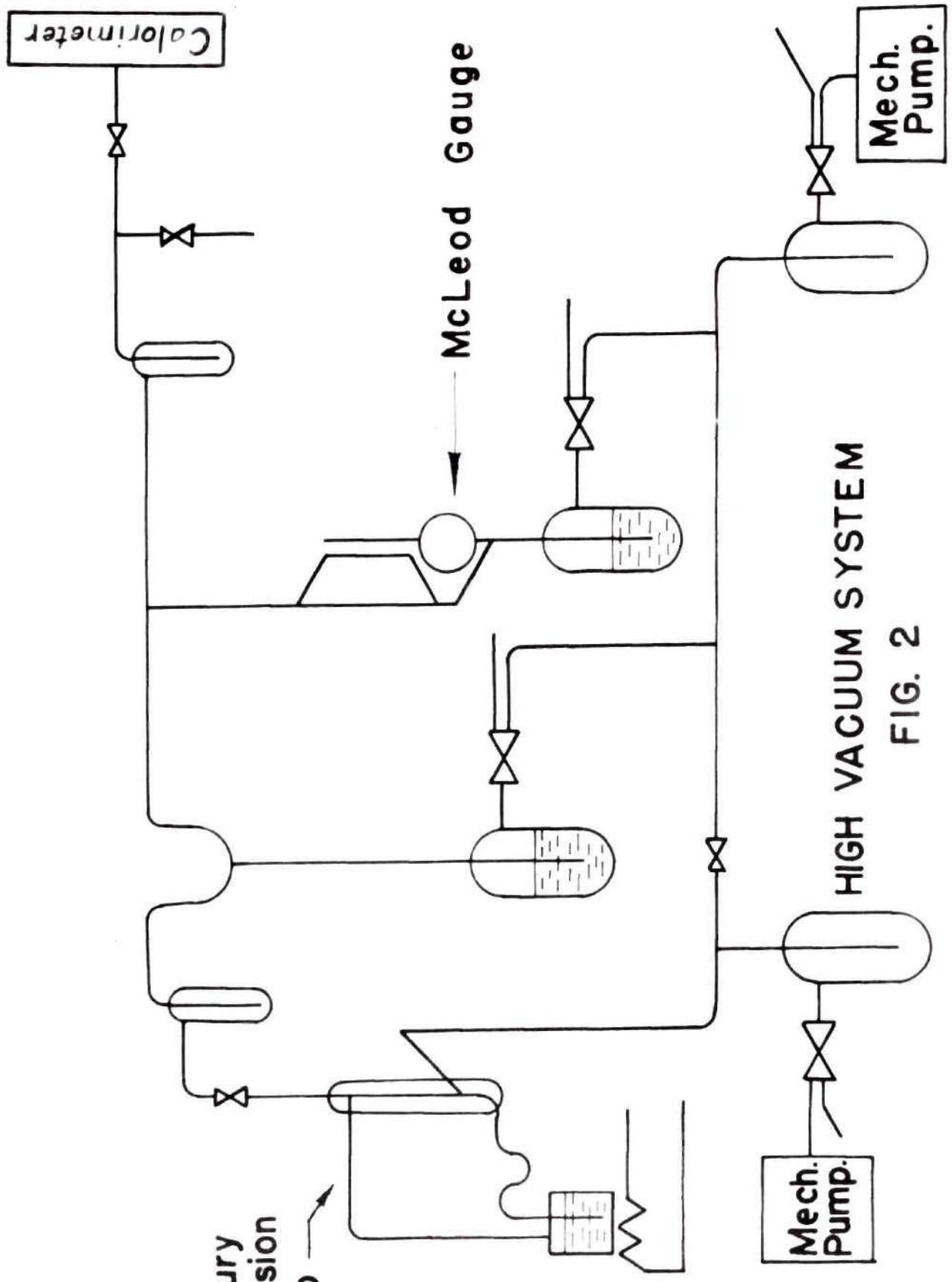
The outer can, C, is a cylindrical brass case which completely encloses the calorimeter can, the copper adiabatic shield, and the aluminum stabilizer shield. It is made of 4" o. d. seamless brass tubing, is 8" long and has a 0.040" thick wall.

The top is soldered on the outer can with ordinary soft solder and is a vacuum tight seal. In the center of the top is connected a 3/4" Inconel tube, A. A monel ferrule, B, is brazed to the top with Harmon and Handy Easy-Flo brazing alloy and the tube is brazed to the monel ferrule. All of the electrical leads pass up through this tube from the calorimeter assembly. The low heat conductivity characteristic of Inconel metal makes its use desirable. Heat losses along this connection from the

calorimeter assembly to the vacuum system is thereby minimized. The Inconel tube connects the space inside the outer can, with the exception of the space inside the calorimeter can, to a high vacuum system which maintains a pressure 10^{-6} mm. Hg. or lower. The outer can acts as the vacuum jacket for the calorimeter assembly.

The insulated box in which the entire assembly is placed is made of sheet metal sides with plywood top and bottom. It is cylindrical and has these dimensions: 8 1/2" diameter and 12" long. Inside this box are placed rings of Celotex which act as an insulating material. The outer can is entirely surrounded by at least 2" of Celotex.

The Inconel tube goes into a header 30 inches from the calorimeter assembly. The header is rectangular and made of the same material. From the header pass two 3/8" copper tubes 4" long and one 1/2" Inconel tube 12" long. The two copper tubes carry the heater and the thermocouple wires which are here separated into two sets for easier identification and manipulation. The last 1/2" of the copper tubes are filled with Central Scientific Co. Sealstix to seal the opening vacuum tight. All of the wires pass through this Sealstix seal and then to terminal blocks mounted just above the header. The Inconel tube is connected to the vacuum system proper. This is accomplished by a glass-to-metal seal made with the same Sealstix. Figure 2 shows the detailed layout of the vacuum system, and Appendix A, Figure 11, is a photo-



HIGH VACUUM SYSTEM

FIG. 2

graph of the vacuum equipment.

The vacuum system contains two glass stopcocks and one U-tube that may be filled with mercury. These "valves" are useful in "breaking" the system into smaller parts for the purpose of testing for any leaks that develop. Thus a leak may be traced to the calorimeter assembly, the middle portion of the system, and roughly the last one-third of the system by proper manipulation of the stopcocks and U-tube.

Two liquid nitrogen traps are incorporated, one near the connection to the calorimeter assembly and the other just before the mercury diffusion pump. These traps are placed in Dewar flasks containing liquid nitrogen. Thus temperatures of the order of 80° K. are maintained in these traps. Condensible vapors are thereby removed from the system making possible the maintenance of low pressures in the calorimeter assembly. Mercury is the chief vapor present and its vapor pressure of 10^{-3} mm. Hg. at room temperature would limit the lowest pressure attainable.

A "Vorpumpe" of the box type manufactured by the W. M. Welch Mfg. Co., Chicago, and called the "Duo Seal Vacuum Pump" is used. Pressures of the order of 5×10^{-4} mm. Hg. are readily attainable. The capacity of the pump is such that a pressure of 10^{-2} mm. Hg. is reached in approximately 10 minutes.

A mercury diffusion pump which is essentially the type designed by Langmuir is used to attain the lowest pressures of 10^{-6} mm. Hg. or lower.

A McLeod gauge is used to measure the low pressure. Its range is from 5×10^{-3} mm. Hg. to 1×10^{-7} mm. Hg. Mercury is allowed to rise from a reservoir by slowly venting the reservoir to the atmosphere. As the mercury rises it cuts off 304 c.c. of gas and compresses it into a capillary whose radius is 0.300 mm. At the same time mercury rises in a capillary tube which is parallel to the gauge. The difference in height is then the pressure of the compressed gas. Boyle's law may be used to calculate the initial pressure of the cut-off 304 c.c., and this pressure is the pressure in the system. The second capillary is used to avoid error due to capillarity.

It is necessary to be able to remove the mercury from the McLeod gauge bulb and capillary as well as the U-tube "valve". A Cenco Hyvac box type mechanical vacuum pump is provided for this purpose. By manipulation of two-way stop-cocks, both the U-tube and McLeod gauge may be opened either to the atmosphere or the vacuum pump in order to raise or equalize the mercury levels.

A special high-vacuum stopcock grease of low vapor pressure has been used with good results. It is No. 15522-A Vacuum Pump stopcock grease sold by Central Scientific Co.

The vacuum system maintains a pressure of 10^{-6} mm. Hg. or lower in the air gap between the calorimeter can and the various shields. This small amount of air makes the transfer of heat by convection much more difficult and removes a possible source of heat loss from the calorimeter can to its surroundings.

CHAPTER IV

ELECTRICAL CONTROL SYSTEMS

All the controls and measuring instruments, except stop watches, are electrical. The wires coming from the calorimeter assembly go to a central switchboard and table which contain the instruments and control devices.

Two operators are necessary to make measurements and manipulate the controls. For this reason the controls are divided into a set of primary controls and a set of secondary controls.

These are:

A. Primary Controls

1. Calorimeter can heating circuit

(a) Potentiometric measurements of current and potential.
(b) Variable resistors.
(c) Stop watches for time measurement.

2. Calorimeter can temperature

(a) Potentiometric measurements of copper-constantan thermocouples located in calorimeter can.

B. Secondary Controls

1. Adiabatic Shield

(a) Variable resistors to regulate heating rate on heating circuits.
(b) Difference thermocouple between calorimeter can and adiabatic shield and between top, bottom, and body of the adiabatic shield as measured by galvanometer scale deflection.

2. Aluminum Stabilizer Shield

(a) Variable resistors to control heating circuits.
(b) Difference thermocouple between adiabatic shield and aluminum shield as indicated on galvanometer scale.
(c) Potentiometric measurement of thermocouple on top of aluminum shield.

A list of instruments showing their serial numbers and use is given in Appendix B, Table VIII.

A photograph of the switchboard and instruments may be found in Appendix A, Figure 12.

There are four constantan and twenty-four copper wires coming from the calorimeter assembly of which two constantan and one copper wires are spares. The other two constantan wires, one of which is connected to the thermocouple inside the calorimeter can and the second which is connected to the thermocouple on top of the aluminum stabilizer shield go directly to an ice junction. The ice junction is made in a dewar flask which is filled with cracked ice and distilled water. A block of clear ice is used to furnish the ice in the ice junction. It is believed that this kind of ice is of a high purity. The constantan wires are soldered separately to #32B. and S. gage D. S. enameled copper wire for the cold junction. These junctions are placed in two glass tubes, partially filled with commercial mineral oil and inserted into the ice bath.

The two copper leads are then connected to terminal

blocks. The difference thermocouple and heating wires are also connected to the terminal blocks. From this point on to all the control instruments, the wires are #18 B. and S. gage type P. D. 1-32 Buna Glazed Copper.

PRIMARY CONTROL CIRCUITS

The primary system contains the controls for making the measurements of calorimeter can temperature, resistance thermometer current and potential measurements, current and potential measurements for the heat added to the calorimeter can, and the time of heating.

The secondary system contains all the difference thermocouples, adiabatic and stabilizer shield heaters, and the thermocouple on top of the aluminum stabilizer shield. The operator of the secondary circuits controls all the shield heaters so as to maintain zero temperature differences between all the difference thermocouples.

It was anticipated that the calorimeter can heater might be useful as a resistance thermometer in making temperature measurements. For this reason the primary set of controls were made to enable the operator to make current and potential measurements and determine the resistance of the calorimeter can heater windings.

Figure 3 is a diagram of the primary control circuits.

LEGEND FOR FIGURE 3

A. Calorimeter Can Heater

B. Resistance equivalent to Calorimeter Can Heater

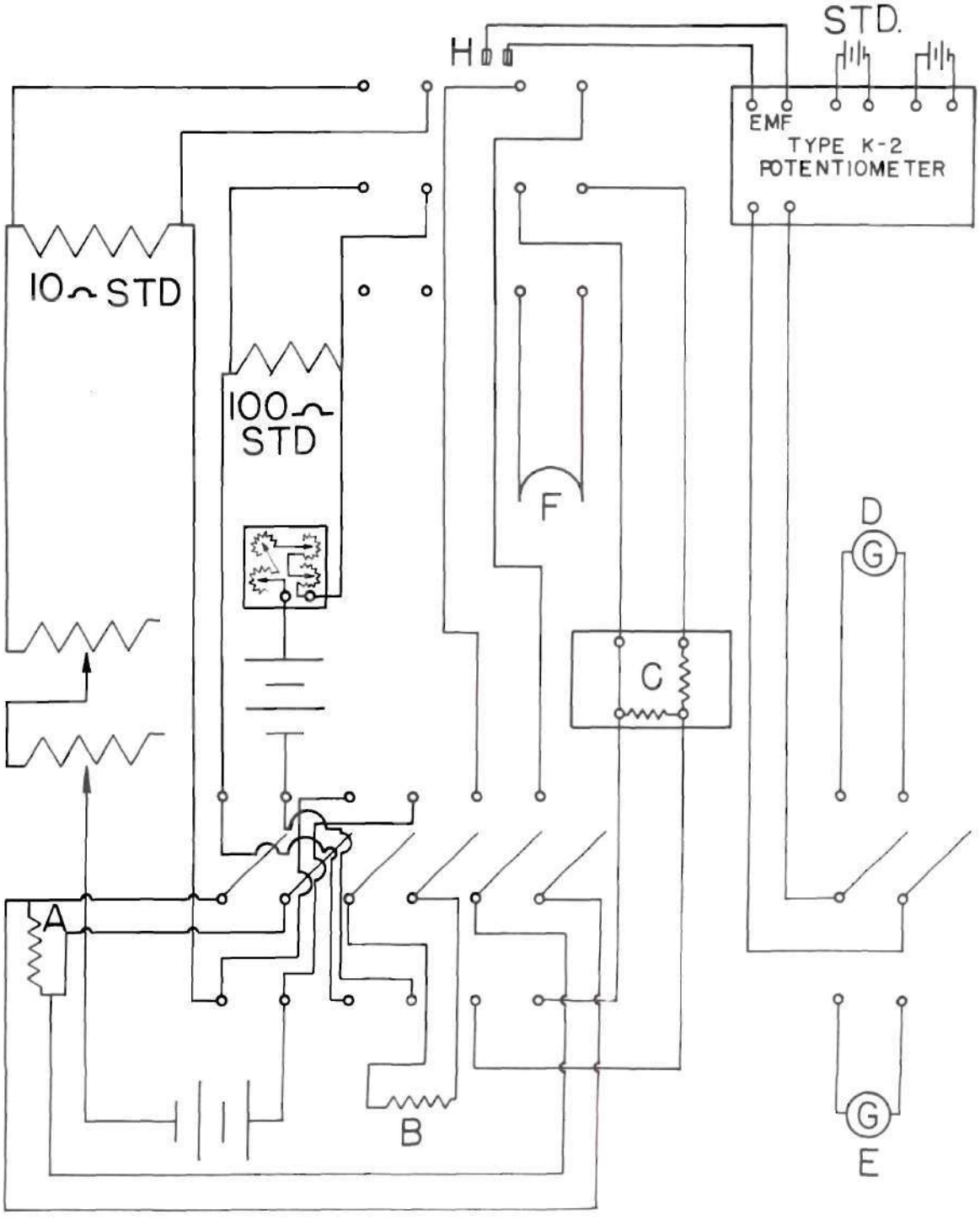
C. Volt Box

D. Type HS (High Sensitivity) Galvanometer

E. Low Sensitivity Galvanometer

F. Main Thermocouple in Calorimeter Can

H. Plug for connecting Potentiometer emf leads to desired contacts



PRIMARY CONTROL CIRCUITS
FIG. 3

Three double-pole-double-throw knife switches are connected together making in effect a six-pole-double-throw switch. This switch controls the calorimeter can heating circuits, and the resistance thermometer circuits. A double-pole-double-throw switch connects either of two galvanometers to the potentiometer. Two double-pole-double-throw knife switches have been modified so as to make three pairs of contacts on each switch. These contacts will be called the potentiometer contacts. One contact blade has been modified so that it may be inserted into any pair of contacts. The contact blade is connected to the emf leads from the potentiometer. In this way the potentiometer may be quickly switched to any pair of contacts for measurements.

The six-pole-double-throw switch is in the down position during the period when the calorimeter can is being heated. The calorimeter can current and potential leads are then connected to the potentiometer contacts and the resistance thermometer battery is connected to a ballast circuit of the same resistance as the resistance thermometer circuit.

The calorimeter can current leads are connected through a twelve volt storage battery and thence through two variable resistors. The circuit is completed through a 10 ohm standard resistor from which a pair of leads is taken to the potentiometer contacts. The twelve volt battery is made by Exide, type 10 BTMH. They are of 6 ampere hours capacity and have a maximum discharge rate of 0.5 ampere. This battery has a

relatively constant discharge rate. The variable resistors are Jagabi rheostats. One rheostat is rated at 875 ohms and 0.7 ampere and the other is 110 ohms and 2.3 amperes. The potentiometric measurement of the potential drop across the 10 ohm standard resistor gives the current flowing through the resistor by dividing the measured emf by a factor of 10.

The calorimeter can potential leads are connected through a Leeds and Northrop volt box to the potentiometer contacts. The volt box is necessary in this circuit since the potentiometer can measure potentials not greater than 1.6 volts.

When the switch is in the upper position, the calorimeter can storage battery is connected to a ballast circuit of equivalent resistance to the calorimeter can heating circuit and the resistance thermometer circuit is connected to the battery and the current and potential leads are then connected to the potentiometer contacts. The resistance thermometer current leads are connected to a 2 volt battery of the type described above, and thence through a 4-dial resistance box and the circuit is completed through a 100 ohm standard resistance. The potentiometer contacts are connected across the 100 ohm standard resistance, which is the same type standard resistance described in the preceding paragraph. The potentiometrically measured emf divided by 100 then gives the current in amperes flowing in the circuit.

The resistance thermometer potential leads are connected directly to the potentiometer contacts since it is not expected that this measured emf will exceed 1.6 volts.

The leads from the thermocouple inside the calorimeter can are connected directly to one pair of potentiometer contacts.

The sixth pair of potentiometer contacts are dead and the contact blade is ordinarily kept in these contacts when no measurements are being made.

The potentiometer is a type K-2, Leeds and Northrop Co., and is an instrument of high precision. A standard cell made by the Eppley Laboratories is used with the potentiometer. It is a cadmium cell of the unsaturated type with a negligible temperature coefficient within the ordinary range of room temperature. A Willard 2 volt low discharge storage battery is used as a current source for the potentiometer.

Two galvanometers are available. One is of a relatively low sensitivity, 3.2 microvolts per millimeter at 1 meter distance from scale, and is used to approximately balance the potentiometer when the magnitude of the emf to be measured is unknown. This prevents possible damage to the other galvanometer which is a type HS (high sensitivity) made by Leeds and Northrop Co. A lamp and scale reading device is used with the type HS galvanometer. The type HS galvanometer has a sensitivity of 0.32 microvolts per mm. This galvanometer is used to make the final adjustment in balancing the potentiometer.

SECONDARY CONTROL CIRCUITS

The secondary control circuits are shown in detail in Figure 4. There are five pairs of variable resistors which control the various heaters B, C, D, E, and F, in the calorimeter assembly. Each of the four difference thermocouples H, J, K, and L, may be impressed alternately across the galvanometer by means of an automatic switch, M, described below. Signal lights, N, on the control panel indicate which difference thermocouple is currently being read on the galvanometer scale. Leads from the four difference thermocouples which by-pass the automatic switch are also connected to the same type of potentiometer contacts as described in the primary control circuits. A pair of leads from the thermocouple on top of the aluminum shield are also connected to potentiometer contacts. A four-pole-double-throw switch may be operated to switch the galvanometer either to the difference thermocouple circuits or to the potentiometer where the emf of the thermocouple on top of the aluminum shield or the emf of each of the difference thermocouples may be measured by the potentiometer.

Table I shows which heaters are used to control the temperature so that the difference thermocouples indicate temperature differences of zero.

LEGEND FOR FIGURE 4

SECONDARY CONTROL CIRCUITS

A. Thermocouple on top of Aluminum Stabilizer Shield

B. Heater on bottom of Copper Adiabatic Shield

C. Heater on body of Copper Adiabatic Shield

D. Heater on top of Copper Adiabatic Shield

E. Heater on body of Aluminum Stabilizer Shield

F. Heater on top of Aluminum Stabilizer Shield

H. Difference Thermocouple between Aluminum Stabilizer Shield and Copper Adiabatic Shield

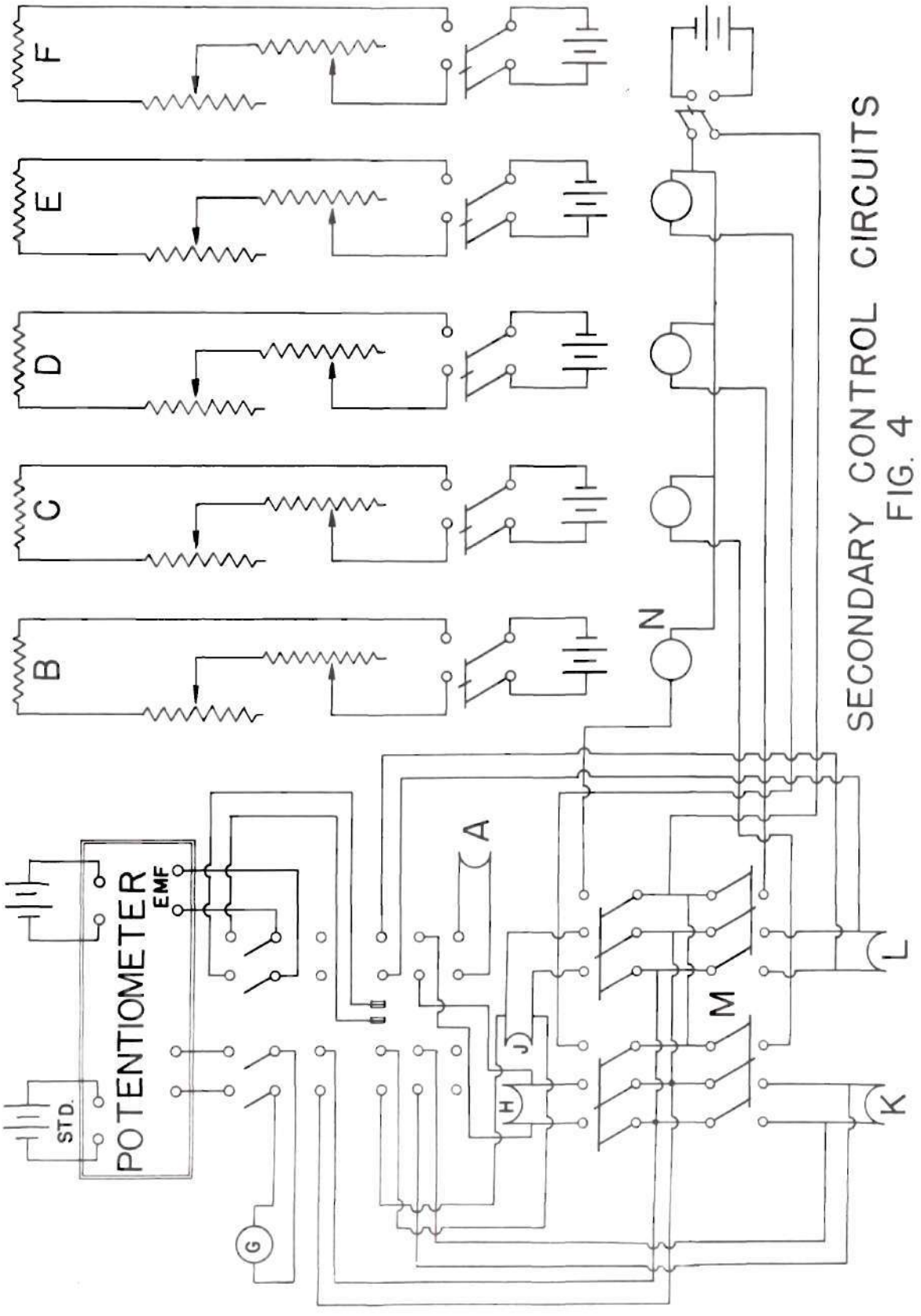
K. Difference Thermocouple between Copper Adiabatic Shield and Calorimeter Can

J. Difference Thermocouple between bottom and body of Copper Adiabatic Shield

L. Difference Thermocouple between top and body of Copper Adiabatic Shield

M. Automatic Switch

N. Signal Lights



SECONDARY CONTROL CIRCUITS
FIG. 4

TABLE I

HEATERS AND DIFFERENCE THERMOCOUPLES

Heater in the Calorimeter Assembly	Difference Thermocouple Controlled
Bottom of the Copper Adiabatic Shield	Between the bottom and body of the Copper Adiabatic Shield
Body of the Copper Adiabatic Shield	Between the body of the Adiabatic Shield and the Calorimeter Can
Top of the Copper Adiabatic Shield	Between the top and body of the Adiabatic Shield
Body of the Aluminum Stabilizer Shield	Between the body of the Aluminum shield and the body of the copper Adiabatic Shield
Top of the Aluminum Shield	Between the top of the Aluminum Shield and the ice junction.

Two variable resistors in series are installed in each heating circuit. They are Jagabi "Lubri-tact" rheostats. One of the pair has a resistance of approximately 800 ohms and the current capacity of 0.8 ampere. The other rheostat has a resistance of approximately 100 ohms and a current carrying capacity 3.8 amperes and is equipped with a screw drive for making fine adjustments. Each heating circuit has its own storage battery and a double-pole-single-throw toggle

switch. The storage batteries are type 10-BTMH made by Exide which was described in the primary control circuits.

Appendix A, Figure 13, is a photograph of the automatic switch. The automatic switch has two cams which rotate at a slow speed and operates the switches in sequence. The motive power is a small alternating current motor which is geared down to rotate the shaft on which the cams are mounted at a speed of 1 rpm. The cams are cylinders which have an eccentric surface on one-fourth of their circumference. This eccentric surface operates, at any one time, three contacts of one switch. The cams are so adjusted that only one switch is closed at a time. In this way each switch is closed approximately fifteen seconds during each minute. Since the period of the galvanometer is seven seconds, there is ample time for a reading to be made. Each switch contains three pairs of contacts which are insulated from the framework of the assembly and from each other. Two pairs of contacts connect the difference thermocouple leads and the other pair connects to one lead of the signal light. One pair of leads go from the automatic switch to the four-pole-double-throw switch on the control panel and four pairs of leads come from the four difference thermocouples inside the calorimeter assembly to the automatic switch. One wire comes to the automatic switch from a 6 volt storage battery which furnishes the current for the signal lights. As each switch is closed this

battery wire is connected through the appropriate signal light on the control panel to the other battery terminal. The signal lights are mounted on the control panel with the appropriate light under each pair of variable resistors. Therefore when the signal light is lighted the operator can ascertain at a glance which resistor should be adjusted. The connections are made such that if the galvanometer deflects on the scale to the left the resistance should be decreased.

A Leeds and Northrop type K-2 potentiometer is used together with a Eppley standard cell. This is the same kind of equipment as described in the primary control circuits. The galvanometer leads from the potentiometer are connected to one side of the four-pole-double-throw switch. The emf leads are connected to one pair of middle contacts in the same switch.

When the four-pole-double-throw switch is in the up position, the galvanometer is connected to the potentiometer and the emf leads from the potentiometer are connected to the contact blade which may be placed in any pair of the potentiometer contacts. In this position the potentiometer may be used to measure the emf of any of the difference thermocouples or the thermocouple on top of the aluminum stabilizer shield.

In the down position, the switch connects the galvanometer directly to one of the difference thermocouples as governed by the automatic switch. The emf leads from the

potentiometer are disconnected from the extension leads to the contact blade so that short circuits may not develop between any of the difference thermocouples and no emf may be impressed on the potentiometer which may not be ascertained since no galvanometer is connected to the potentiometer.

The galvanometer is a Leeds and Northrop type HS and has a sensitivity of 0.32 microvolts per mm with the scale at one meter distance.

There are six pairs of potentiometer contacts to which the four difference thermocouples and the one thermocouple are connected.

CHAPTER V

CALIBRATION OF MAIN THERMOCOUPLE

A copper-constantan thermocouple was used to measure the temperature differences in the calorimeter in the range of 20°C to 150°C. The couple was constructed of B. and S. No. 32 copper-constantan wires. The thermocouple was calibrated using several known transition points; e. g., melting point, boiling point, etc.. A series of values of emf vs temperature was determined in this manner and an equation was fitted to these points for interpolation of temperature points when the emf values are known.

Two primary standards were used: the boiling point of water and the melting point of tin. The tin was a standard sample secured from the National Bureau of Standards and had a certified melting point of 231.9$_0$°C. Three secondary standards were chosen: the transition of $Na_2SO_4 \cdot 10\ H_2O$ crystals at 32.384°C[6], the melting point of naphthalene at 80.01°C[7], and the melting point of benzoic acid at 122.375°C[8].

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(6) International Critical Tables, McGraw Hill Book Co., for the National Research Council, (1926), p. 54, Vol. 1

(7) Gustav Egloff, Physical Constants of Hydrocarbons, Vol. IV, Reinhold Publishing Corp., New York, (1947), p. 77

(8) F. W. Schwab and Edward Wichers, Journal of Research of the National Bureau of Standards, RP1647, (1946)

These points were fitted to an equation of the form

$$E = at+bt^2+ct^3 \qquad (9)$$

where E is the emf of the thermocouple, t is the temperature in °C and a, b, and c are constants. Three of the five points were used in calculating the equation and the other two points were used as check points. Using the above equation a temperature-emf table was constructed and used to convert the potentiometer readings of emf of the thermocouple to degrees centigrade.

THE FREEZING POINT OF NAPHTHALENE

It was anticipated that naphthalene would be used as the first sample whose heat capacity was to be measured. A sample of high purity was, therefore, necessary. Baker's "Naphthalene by Alcohol" was subjected to the following purification: About 200 grams of naphthalene was dissolved in 95% ethyl alcohol. This mixture was refluxed on a water bath until complete solution took place. After setting for ten minutes about 90% of the solution was decanted into another vessel and allowed to cool. The crystals were filtered through a Buchner funnel and washed with cold alcohol.

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(9) W. F. Roeser and H. T. Wensel, Journal of Research of the National Bureau of Standards, RP768, 14, p. 271, (1935)

The crystals were dried on the suction filter for three or four hours. This procedure was carried out three times except that on the second and third recrystallizations the mixture was cooled in an ice bath before filtering. After the final filtration the crystals were dried for approximately 18 hours on the suction filter with no alcohol in the filter flask. The crystals were then substantially dry. The alcohol filtered off on the first recrystallization was very brown but the third filtrate was clear.

The recrystallization procedure was followed by two vacuum sublimations. The apparatus used consisted of three 600 cc. flasks connected to a glass manifold which was in turn connected through a stopcock to a dry ice-alcohol trap and thence to a high vacuum system. The recrystallized product was placed in the first flask and the glass seal made. The sample could then come in contact only with glass. The system was evacuated to approximately 5×10^{-3} mm. Hg. pressure. About 10% of the naphthalene was sublimed from the first to the second to the third flasks and to the cold trap thus "washing" the system and removing volatile impurities. The second flask was immersed in a dry-ice alcohol bath and the first flask was heated. This procedure sublimed the naphthalene to the second flask. About 25% of the naphthalene was left in the first flask. The process was repeated and about 75% of the naphthalene was sublimed to the third flask.

The glass neck was broken by making a file mark around it and placing a red-hot end of a glass rod on the mark. The naphthalene was melted and poured into the heated calorimeter can and the balance was poured into a bottle.

Considerable difficulty is encountered if the naphtha- is sublimed too fast. Naphthalene condenses throughout the entire apparatus. Heating the whole apparatus except the cold flask alleviates the situation.

The calorimeter was assembled with the purified naphthalene in the calorimeter can and the vacuum system maintained at about 10^{-5} mm. Hg. absolute pressure.

The emf of the thermocouple at the melting point was determined by melting the sample and also by freezing. Since freezing points are in general more satisfactory[10], the data for the freezing point will be used. However, since the thernal head on the sample can be controlled easily, excellent agreement between the freezing point and melting point of naphtha- was found. The emf of the two points differed only by 0.1 microvolt or 0.002_4°C.

The melting point was found by applying heat to the calorimeter can via the constantan heater wound on the can and at the same time controlling the adiabatic shield so that its temperature was approximately that of the can. The emf of the thermocouple in the can was read and the time noted.

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(10) W. F. Roeser and H. T. Wensel, Journal of Research of the National Bureau of Standards, RP768, 258, 14, (1935)

A plot was made of emf vs temperature and the constant emf determined.

While the naphthalene was melting the following observations were made:

1. Doubling the rate of heating increased the temperature of the sample. If the battery was 6 volts and it was increased to 12 volts, the temperature of the naphthalene increased about 0.1°C.

2. With the calorimeter heat off and the adiabatic shield maintained at 4°C colder than the can, the can temperature remained unchanged for two hours.

The freezing point was determined in a manner similar to the melting point. The melted naphthalene was cooled by maintaining the adiabatic shield colder than the can and the emf read and the time noted. The thermal head from the calorimeter can to the copper adiabatic shield could easily be controlled by controlling the heaters on the adiabatic shield. Various thermal heads were used and their effect on the can temperature could be seen from the plot of calorimeter can temperature vs time. The naphthalene was frozen over a period of three to four hours during the runs that were made.

When the adiabatic shield was maintained 5 to 6°C colder than the can for periods of thirty minutes, the can temperature remain unchanged. At various times during freezing the adiabatic shield was brought to the temperature of the can for thirty minutes so that thermal equilibrium

could be established in the calorimeter can. The temperature of the naphthalene during these periods were found to be the same as when the adiabatic shield was 5°C colder. The plot of emf vs time showed a constant temperature for as long as four hours. A typical curve is given in Appendix A Figure 14. The change of slope of the curve at the beginning and ending of freezing and melting was very sharp and was indicative of a very pure sample.

Four runs made on the purified naphthalene sample gave results of:

TABLE II

FREEZING POINT OF NAPHTHALENE

E - micro-volts	Run No.
3122.5	1
3122.6	2
3122.2	3
3122.6	4

A tendency to supercool during cooling was noted. However, when supercooled 3° to 5°C a slight tap on the calorimeter seemed to start freezing and the temperature of the sample would quickly rise to the constant point.

A sample of Baker's CP Naphthalene was placed in the calorimeter and its freezing point found. This value was 3075 micro-volts which is one degree less than that of the purified

sample.

During these runs with naphthalene the temperature-resistance characteristics of the constantan heater wound on the calorimeter can were found. A change of 1°C of the heating coil made no measureable difference in its resistance, so it was concluded that the resistance of constantan is not sufficiently sensitive to temperature change as to be useful here as a resistance thermometer.

THE FREEZING POINT OF BENZOIC ACID

The melting point of benzoic acid was used to find the next temperature-emf point. A sample had been procured from the National Bureau of Standards for this purpose. However, this sample was not used in the final determinations due to trouble in preliminary tests.

The benzoic acid was loaded into the calorimeter can, the calorimeter assembled and vacuum pulled. A test melting and freezing determination showed no constant emf as noted in the previous determination with naphthalene. For this reason the calorimeter was disassembled and inspected.

The reason for the failure of the determination was readily apparent. First, the solder seal on top of the calorimeter had failed. This was attributed to the fact that on this one experiment ordinary soft solder was used and the temperature of the calorimeter can has been raised to about 160°C in an attempt to locate the melting point. Apparently

soft solder does not make satisfactory seals to be used under high vacuum at these temperatures. Also, the benzoic acid had taken on a green color that gave a copper test with the ferro-cyanide ion. Subsequent tests showed that both benzoic acid and salicylic acid will turn green when melted in the presence of copper. This experience proved conclusively that the gold plating on the copper can was either porous or had failed sufficiently to allow the sample to contact the copper of the can. So it was evident that if benzoic acid were to be used, the thermocouple would have to be removed from the calorimeter can and calibrated in other vessels.

The National Bureau of Standards benzoic acid sample having been used up in the preceding experiments, it was necessary to obtain another purified sample. About 225 grams of Baker's "Benzoic Acid-Sublimed" was re-sublimed in vacuo into the following vessel: A piece of 3.6 cm. I. D. pyrex glass tubing 8 cm. long closed at one end and the other end fused to a 15 cm. long piece of 5 mm. I. D. pyrex glass tube. A protection tube was made of pyrex glass which was about two millimeters inside diameter. A few drops of mineral oil was placed in the protection tube and the thermocouple inserted into the oil. The thermocouple junction (inside the protection tube) was immersed in the benzoic acid to a depth of 2.5 cm. and the melting point vessel placed in a stirred oil bath. The oil bath temperature was controlled by a bunsen burner

placed under the oil bath.

The general procedure for obtaining the freezing point data was this: The oil bath was maintained at 130°C until all the solid had melted. The bath was then cooled to below 122°C as indicated by a mercury thermometer immersed in the oil bath. The sample tended to supercool but stirring or dropping a crystal of the benzoic acid into the liquid was sufficient to begin freezing.

When the oil bath temperature was varied during freezing the temperature of the freezing liquid was changed. If the oil bath was varied from 2° to 10°C colder than the sample, the sample temperature was depressed about 0.1°C. The oil bath temperature was controlled to ± 1°C and that of the benzoic acid was constant to about ±0.01°C. A plot of the data was made and the average value of the benzoic acid during freezing was used.

TABLE III

FREEZING POINT OF BENZOIC ACID

Ave. emf-microvolts	Ave. oil bath temperature °C
4957.7	115
4959.0	119
4961.9	121

As shown by the above values, as the oil bath was maintained nearer the melting point temperature, the sample

temperature increased slightly. The difference between the lowest and highest values of sample temperature are 0.093°C. It is reasonable to expect that the effect of the oil bath temperature and the effect of any impurities would be to depress the freezing point, and since these are the only possible variables present, the highest value of 4961.9 micro-volts was used.

Thought was given to the possibility of using salicylic acid as a check point, however there turned out to be two reasons which prohibit its use. The fact that melted salicylic acid will react with copper made it unsuitable for use in the calorimeter can. Also when attempts were made to purify the acid by sublimation in vacuo, it was found that some decomposition occurred. A test run was made on a sample of Baker's "Salicylic Acid CP grade" with no further purification. Three runs under the same conditions of oil bath temperature showed marked decrease in the freezing temperature and the sample had the odor of phenol, indicating decomposition had taken place. For these reasons, it was decided that for this purpose the freezing point of salicylic acid was unsatisfactory.

THE TRANSITION OF SODIUM SULFATE

The decahydrate of sodium sulfate loses all its water

of hydration at 32.384°C. This phase change occurs at this temperature in concentrations above approximately 33% Na_2SO_4 [11] and it is therefore necessary to insure that sufficient anhydrous salt is present during the determination. Baker's CP $Na_2SO_4 \cdot 10\ H_2O$ crystals, to which had been added a few grams of the anhydrous salt, were melted and placed in a one quart dewar flask. A protection tube, one end of which had been drawn out to about two millimeters inside diameter, was immersed at least 10 cm. into the mixture of Na_2SO_4 and solution. The protection tube contained sufficient mineral oil so that the thermocouple junction was immersed to a depth of about two centimeters.

As the mixture slowly cooled in the dewar flask, the emf of the thermocouple was followed at intervals of one to three minutes at the beginning of transition and at intervals up to ten minutes when the emf became constant. The emf was constant over a period of three hours when the determination was stopped.

When the data were plotted the average emf during the constant period was found to be 1200.4 micro-volts. A variation of about 0.1°C occurred as the phase change took place and this variation seemed to be directly associated with the

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(11) O. A. Hougen and K. M. Watson, Industrial Chemical Calculations, Second Edition, John Wiley and Sons, Inc., p. 338, (1936).

frequent stirring of the mixture. The stirring was done with the protection tube. Over periods of ten minutes when no stirring was done the variation was less than 0.01°C.

THE BOILING POINT OF WATER

The steam point was next used as a calibration point. A 500 cc. distilling flask was well lagged with rope asbestos down to the bulb. Three hundred cubic centimeters of distilled water was placed in the flask and a water condenser connected on the distilling arm. A protection tube of about two millimeters inside diameter and containing mineral oil as in the other determinations was inserted to a point about one centimeter below the distilling arm exit and held in place with a rubber stopper. The thermocouple junction was then in the path of the water vapor just before it left the flask. An asbestos and wire gauze was placed under the flask and the flask was heated by a bunsen burner.

The distilled water was brought to near the boiling point and then the heat adjusted until the water barely would bubble. The emf of the thermocouple was measured with respect to time until the emf no longer changed. The heat was then increased several times but no significant change was noted in the emf of the thermocouple. This constant period was held over a period of thirty minutes when the water level inside the flask became too low.

The constant emf was found to be 3956.6 micro-volts with a variation of ±0.02°C.

During the course of the experiment the barometric pressure was read and found to be 747.55 mm. Hg. Roeser and Wensel[12] give the relation between the temperature, t, in °C and the pressure, p, for the range 680 to 780 mm. of Hg. as:

$$t = 100.000 + 0.0367\ (p - 760) - 0.000023\ (p - 760)^2 .$$

Use of this equation gives the boiling point of water to be 99.537°C at 747.5 mm. of Hg.

THE FREEZING POINT OF TIN

A sample of tin which was procured from the National Bureau of Standards was used to determine one point above the highest temperature that the thermocouple was to be used. A calibration in the neighborhood of 160°C would have been more desirable but was not available. This sample had a freezing point of 231.90°C as determined by the National Bureau of Standards.

The sample of tin was placed in a pyrex test tube and the surface covered with graphite to discourage oxidation of the metal. A protection tube of the same type as used before was immersed in the molten metal to a depth of about five

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(12) W. F. Roeser and H. T. Wensel, Journal of Research of the National Bureau of Standards, RP768, 14, p. 261, (1935)

centimeters. A test tube was placed in an oil bath and the sample melted. After holding the sample at 10°C above the melting point for ten minutes it was slowly cooled. As the thermocouple emf became constant the oil bath temperature was maintained constant within two degrees.

THE TEMPERATURE - EMF RELATION

The plotted data of emf vs time showed an emf variation of ±2 micro-volts or 0.04°C. The average value during the period of freezing was 10222.0 micro-volts.

Tabulated below are the experimental values of emf vs temperature together with the possible errors. The possible errors were arrived at by taking the actual variation of the emf reading during the phase change and estimating an error due to condition of sample or conditions under which the value was determined. For example, the determination of the steam point is more likely to give a high reading due to superheating the vapor than to give a low reading.

TABLE IV

CALIBERATION POINTS FOR THERMOCOUPLE

No.	Emf - micro-volts	Possible error micro-volts	Temperature °C
1	3122.6	±2	80.01
2	4961.9	±2	122.375
3	10222.0	±3	231.90
4	1200.4	±2	32.384
5	3956.6	±2	99.537

Using points number 2, 3, and 4 the equation of the temperature-emf curve was found to be:

$$E = 35.688\ t + 0.043627\ t^2 - 3.210 \times 10^{-5}\ t^3$$

E = emf in micro-volts
t = temperature in °C

Since the reference junction is 0°C the curve will pass through the origin so that no constant term appears in the equation.

This equation was used to calculate the emf corresponding to the temperatures of points number 1 and 5. The results are tabulated below.

TABLE V

CHECK CALIBRATION POINTS FOR THERMOCOUPLE

Emf - micro-volts experimental	Emf - micro-volts calculated	exp. - calc. micro-volts	exp. - calc. °C
3122.6	3118.3	-4.3	-0.10
3956.6	3952.9	+3.7	+0.08

These data indicate that the equation fits the curve within ±0.1%. Roeser and Wensel[13] state that the copper-constantan thermocouple can be relied upon to retain its calibration within about 0.2°C when used up to 300°C. The calculated equation may then be expected to give values of temperature within 0.1°C in the range to be used in this

(13) Wm. F. Roeser and H. T. Wensel, BS J. Research, RP 768 14, (1935), p. 271

work.

The slope of the equation,

$$\frac{dE}{dt} = 35.688 + 0.087254\ t - 9.630 \times 10^{-5}\ t^2$$

indicated that temperature differences of one degree will change the emf reading in the first decimal so that in constructing a temperature-emf table it will be necessary to tabulate values for each degree to obtain accuracy of 0.1 micro-volt. For values falling in between each degree it will then be necessary only to make a straight line interpolation. Such a table is given in the Appendix B in Table IX.

CHAPTER VI

PROCEDURE IN OPERATING CALORIMETER

The general procedure for making a heat capacity determination is to measure the temperature rise of a weighed sample when a measured amount of heat is added. The data must therefore be taken so that these quantities may be either directly measured or calculated.

Two operators are required in taking the data during a determination or run. One operator will be designated as the primary operator and the other will be the secondary operator. These terms correspond to the division of controls made in Chapter IV. The general duties of the primary operator are to measure the temperatures of the calorimeter can and sample and to measure the heat input to the calorimeter heater. The secondary operator will manipulate the heater controls of the copper adiabatic shield and the aluminum stabilizer shield so as to maintain the various difference thermocouples within the required limits. Sample data sheets are given in Appendix B Table X and Appendix B Table XI which show the data taken by each operator.

The primary operator starts stop watch number 1 at the beginning of the run and as temperature and power measurements are made, the time is recorded to the nearest second. At the beginning and ending of a heating period the time is measured to the tenth of a second.

When the secondary operator has the adiabatic shield at the temperature of the calorimeter can, the preliminary or drift measurements of the temperature of the calorimeter can are made by the primary operator. If the temperature of the can is in a steady state; e. g., constant or changes at a constant rate, the heating period may be started.

As the primary operator closes the switch connecting the battery to the calorimeter can heater he starts stop watch number 2 simultaneously. The secondary operator must also increase the heat input to the adiabatic shield, so that the temperature of the adiabatic shield will follow that of the calorimeter can.

During the heating period several measurements of the current going through the calorimeter can heater and of the potential drop across the heater are made by the primary operator. The secondary operator, in the meantime, controls the heating rate of the adiabatic shield heaters so that they rise in temperature at the same rate as the temperature of the can. He also records the reading of the various difference thermocouples several times during the heating period.

At the close of the heating period, the primary operator simultaneously stops watch number 2, starts watch number 1, and disconnects the battery from the calorimeter heater. He then follows closely the change of the temperature of the calorimeter can. The temperature will continue to rise and then start to decline after the heating circuit is opened.

Closely spaced points of temperature with respect to time are necessary to determine the final temperature of the sample and calorimeter can.

The secondary operator must also reduce the heat input to the shield heaters in order to keep the shield temperature the same as that of the calorimeter can. When these controls are adjusted, the difference couple readings are again recorded.

The primary operator continues to follow the calorimeter can temperature until a steady state is again attained. The procedure may then be repeated for another determination at the higher temperature.

The automatic switch, which connects a difference thermocouple to the galvanometer every 15 seconds proved very useful to the secondary operator. He has numerous controls to maintain during the heating period and this automatic shift of difference thermocouples relieves him of a number of manipulations. The period of the galvanometer is 6 seconds and the space of 15 seconds when the difference thermocouple is connected across the galvanometer is just sufficient time for the correct reading to be made and a rheostat adjusted.

It became apparent after a few test runs that the set of 10 rheostats, two for each heater, could not be individually controlled satisfactorily during the beginning and ending of a heating period when the heat requirements for the heaters were changing rapidly.

This difficulty had been anticipated when the design was made and the three heaters on the adiabatic shield were specified so that they could be operated in series. A change was accordingly made in these heating circuits so that they could be operated either in series or in parallel. Subsequent test runs showed that series operation of these heaters was satisfactory. One pair of rheostats could then be used to control the entire adiabatic shield. In general, the temperature differences between the top and body of the adiabatic shield were 0.03°C with the top being warmer than the body of the shield. Also the bottom of the adiabatic shield was 0.01°C to 0.03°C colder than the adiabatic shield body. These two differences would tend toward cancelling each other since they are of opposite sign.

To further decrease the difficulties of maintaining adiabatic conditions around the calorimeter can, it was found that by not attempting to make the temperature of the aluminum stabilizer shield follow that of the calorimeter can during the heating period allowed the secondary operator to confine his attention to maintaining the temperature difference between the calorimeter can and the adiabatic shield within narrow limits during the beginning and ending of the heating period. This temperature difference is, after all, the critical difference to be controlled since the adiabatic shield is the only one that can "see" the calorimeter can and transfer heat by radiation or convection.

The purpose of the aluminum stabilizer shield is to facilitate control of the adiabatic shield and this is realized by bringing the temperature of the aluminum stabilizer shield to that of the calorimeter can before each heating period and then allowing it to heat slowly but at a lower rate than the calorimeter can during the heating period. The adiabatic shield is then surrounded by a body that never differs from it in temperature by more than 4 to 5°C. The temperature of the adiabatic shield is then nearly dependent on the heat applied to it since a large temperature gradient does not exist between it and its surroundings.

Using these modifications the secondary operator can read the difference thermocouple between the calorimeter can and adiabatic shield continuously during the beginning and ending of the heating period and thereby control this temperature difference during periods of greatest change. Then when a stable condition is attained shortly after beginning of the heating period, the automatic switch is used to read and control the other difference thermocouples.

CHAPTER VII

CALIBRATION OF EMPTY CALORIMETER

The heat capacity of the calorimeter can must be known before other materials can be investigated. Measurements of heat capacity made with the calorimeter: e. g., temperature rise and heat input, include the effect of the calorimeter can and its contents. If, then, the heat capacity of the calorimeter can is known as a function of temperature, the value at the correct temperature may be subtracted from the heat capacity of the calorimeter can and its contents, leaving the value of the heat capacity of the contents or sample.

This calibration of the empty calorimeter will also show some of its operating characteristics. These characteristics include the accuracy to be expected, magnitude of heat losses, specific data needed to make calculations, lags in heaters and thermocouples, effectiveness of controls, and general operability of equipment.

INVESTIGATION OF THERMAL LAGS IN ADIABATIC SHIELD

The effect of various thermal heads on the calorimeter can was determined. This information was desirable in order to determine the limits within which the temperature difference between the adiabatic shield and the calorimeter can could be tolerated.

Table VI shows the results of three such determinations. Typical calculations and procedures are found in Appendix C.

TABLE VI

DRIFT RATE OF CALORIMETER TEMPERATURE

t °C	$\frac{dq}{d\theta}$	$\frac{dt}{d\theta}$ cal. can	Temp. adiabatic shield minus temp. cal. can
44	0.105 cal/min	0.015 °C/min	+ 0.33°C
23.5	0.077 cal/min	0.011 °C/min	+ 0.32°C
23.5	0.035 cal/min	0.005 °C/min	+ 0.14°C

These data show that by maintaining the adiabatic shield temperature within 0.02°C to 0.10°C of that of the calorimeter can, the effect on the calorimeter can temperature would be very small indeed--less than 0.035 calorie per minute.(14)

During steady state conditions, the adiabatic shield temperature may be kept quite easily within 0.02°C of the calorimeter can, but during rapid change conditions, such as at the start or end of a heating period, the can temperature may vary up to a maximum 0.2°C from the adiabatic shield for a few seconds. However, since the time during which this

(14) The gm-calorie is used throughout this paper.

difference exists is small--of the order 30 seconds--the gain or loss of heat is 0.03 calorie or less in a total of about 40 calories.

The adiabatic shield will have opposite effects at the start and end of a heating period. It will lag or be colder than the calorimeter can at the start and be warmer at the end of the heating period. The net error will, therefore, be the algebraic sum of these errors.

The possible error anticipated from this source should be less than one per mille under ideal operating conditions.

The pressure in the calorimeter assembly was approximately 10^{-4} mm. Hg. during the aforementioned determination. It is anticipated that in later work, pressures of the order of 10^{-6} mm. Hg. would be used, but these drift measurements indicated that for this work the vacuum system was satisfactory.

Figure 5 shows the temperature difference between the adiabatic shield and calorimeter can during a run made at 80°C on the empty can. The temperature ordinate has been expanded so that the variation of temperature differences could be easily seen.

At the start of the heating period the calorimeter can became warmer than the adiabatic shield due to the sudden surge of heating. However, within about 15 seconds, the operator can adjust the adiabatic shield to the can temperature. This shows that the adiabatic shield heater responds very quickly to the controls and it is also noted that the time lag between

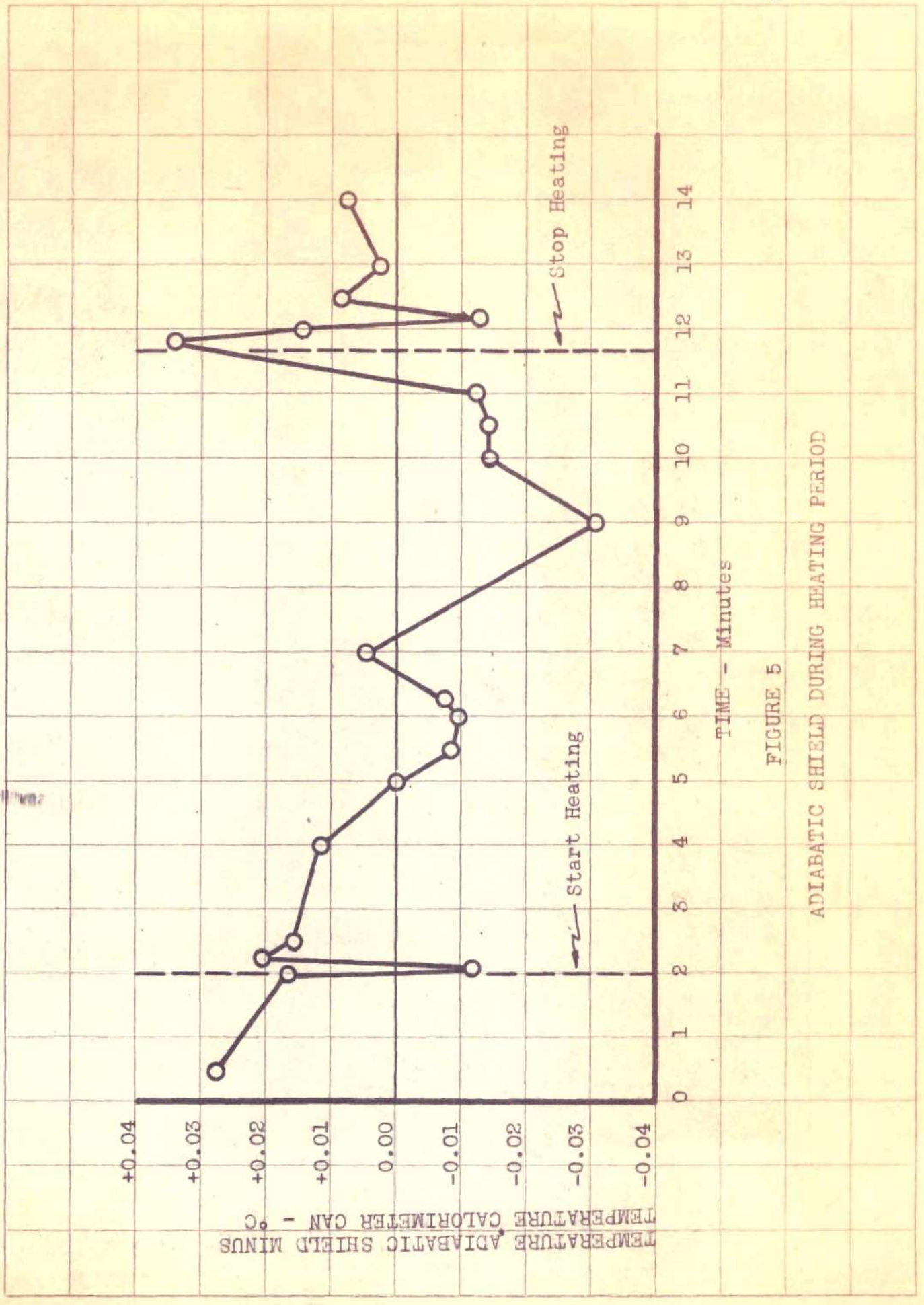

FIGURE 5

ADIABATIC SHIELD DURING HEATING PERIOD

changing the heater control and its effect on the difference thermocouple is of the order of 3 seconds or less. The response of the system to controls is, therefore, considered quite good.

MEASUREMENT OF ENERGY INPUT

The use of a ballast circuit of nearly the same resistance as that of the calorimeter can heater caused the heating rate to be nearly constant. The maximum deviation during a heating period was ordinarily about 0.00035 watts or 0.0050 cal/min., where the heating rate is 0.27 watts.

During each heating period, at least four measurements of current and potential were taken. These data were plotted as a function of time and then by multiplying the values of current and potential at the same instant of time, a curve of power vs time could be plotted. Graphical integration of this curve gives the energy input to the calorimeter can. Appendix A Figure 15 gives a sample calculation of heat input from the tabulated data.

This time of a heating period, approximately ten minutes, was measured by a standard type of stop watch that could be read to one tenth of a second. Two watches were used in these measurements and they were checked against each other over a period of two hours and no deviation was noted. When they were checked against an electric clock, which could be read

to one second, over a period of three hours no deviation could be detected. The measurement of time was, therefore, accurate to ± 0.2 second on each reading which makes the time error liable to a possible error of ± 0.4 second.

MEASUREMENT OF TEMPERATURE RISE

The initial temperature is readily determined. During the initial or "drift" period of a run, the temperature is read until it is constant or a constant change is observed. Then the calorimeter can heater switch is closed. This initial temperature is plotted versus time and the temperature is extrapolated to the starting time. This curve is practically a straight line so that the extrapolation involves very little chance for error.

However the final temperature poses quite a different problem. The curve of temperature versus time at the end of heating is shown in Figure 6. As can be seen from the curve, heating continues for nearly a half minute after the heating circuit is opened. This effect is probably due to the fact that heat must be transferred from the heating coil on the exterior of the calorimeter can to the interior where the thermocouple is. Some temperature gradient exists between these points and this interval represents the time required for heat to be transferred by conduction through the can to the thermocouple. When the calorimeter can contains liquid

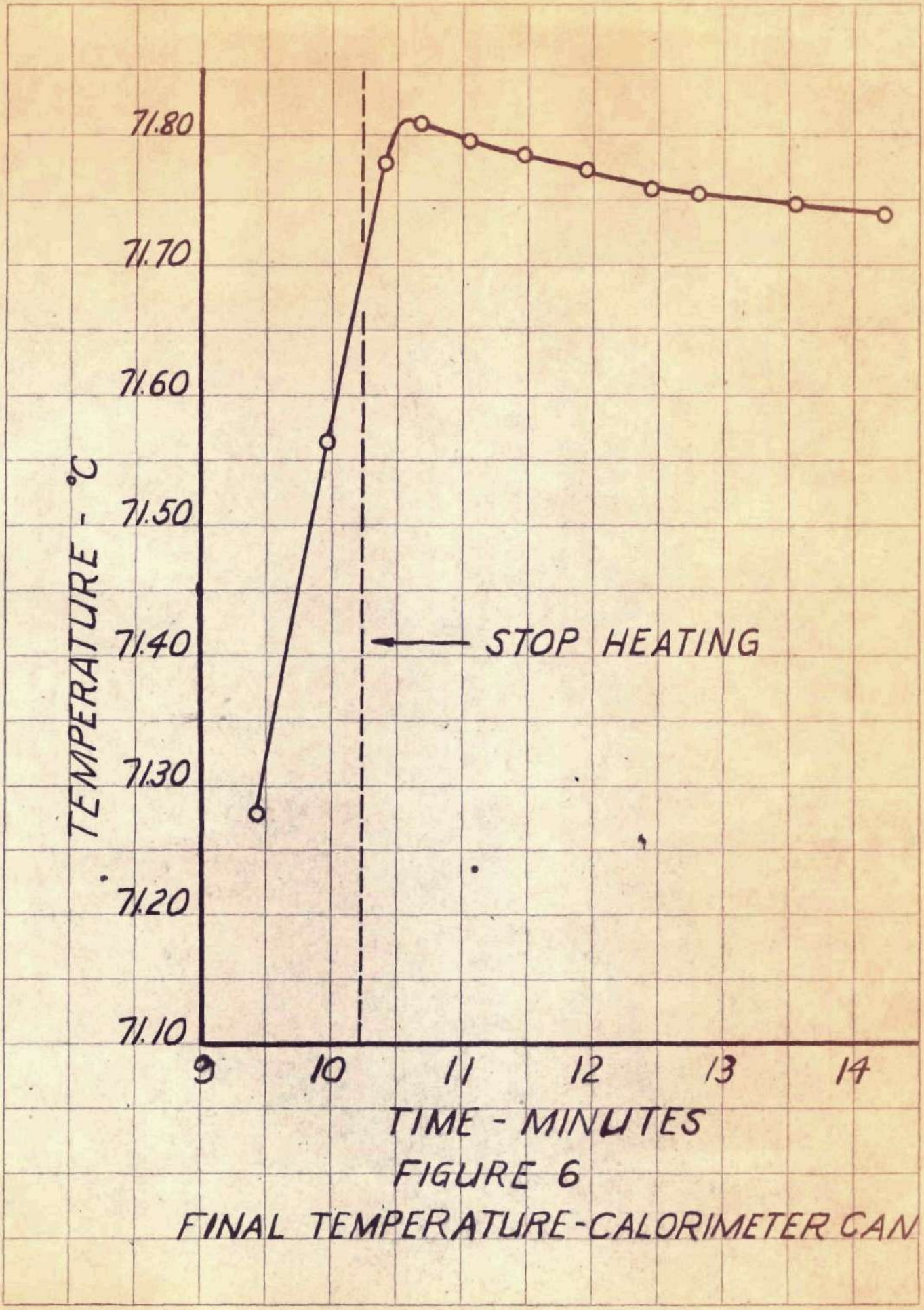

FIGURE 6

FINAL TEMPERATURE-CALORIMETER CAN

naphthalene, the final temperature levels off to a normal drift rate almost immediately. The liquid must contribute to more even heat distribution and reduces temperature lags. The case where the calorimeter can contains either air or solid naphthalene will be considered since nearly all the measurements made were under these conditions.

The final temperature, about 5°C above the initial, is the maximum temperature to which the calorimeter can and contents will be raised by the heat input to the can. Two effects on the can must, therefore, be considered. The first effect is the continued rise in temperature of the calorimeter can and the normal drift of the calorimeter can temperature at the final, steady-state conditions. This final drift rate is noted on the temperature-time graph immediately following the temperature maximum. If, then, this drift rate portion of the curve is extrapolated back to the time at which the heating period ended, the maximum temperature that the calorimeter can would have attained should be located. This is the procedure used in establishing the final temperature.

More chance for error is inherent in determining this final temperature. It is important that closely spaced temperature measurements be made following the end of the heating period so that the slope of the drift portion of the curve can be more precisely determined. The possible error of this extrapolation is at least the upper and lower limits at which the slope may lie. Added to this possible error is the un-

certainty in the temperature measuring instrument, which is taken as ±0.2 micro-volt or approximately ±0.005°C.

Appendix A Figure 16 shows the determination of initial and final temperatures used in the sample calculation of heat capacity in Appendix D.

SUMMARY OF ERRORS

The possible errors involved in a general determination of heat capacity are summarized below. The calculations of errors are given in detail in Appendix E.

A.	Temperature rise	=	± 0.55%
B.	Heat Input	=	± 0.05%
C.	Heat Loss	=	± 0.05%
D.	Total	=	0.55% + 0.05% + 0.05% = 0.65%

This figure of ±0.65% represents the agreement to be expected under normal operating conditions.

HEAT CAPACITY OF EMPTY CALORIMETER CAN

Appendix B Table XII gives the values of 15 determinations of the heat capacity of the empty calorimeter can between 27°C and 148°C. These data are plotted in Figure 7. The curve drawn through the plotted data agree within the

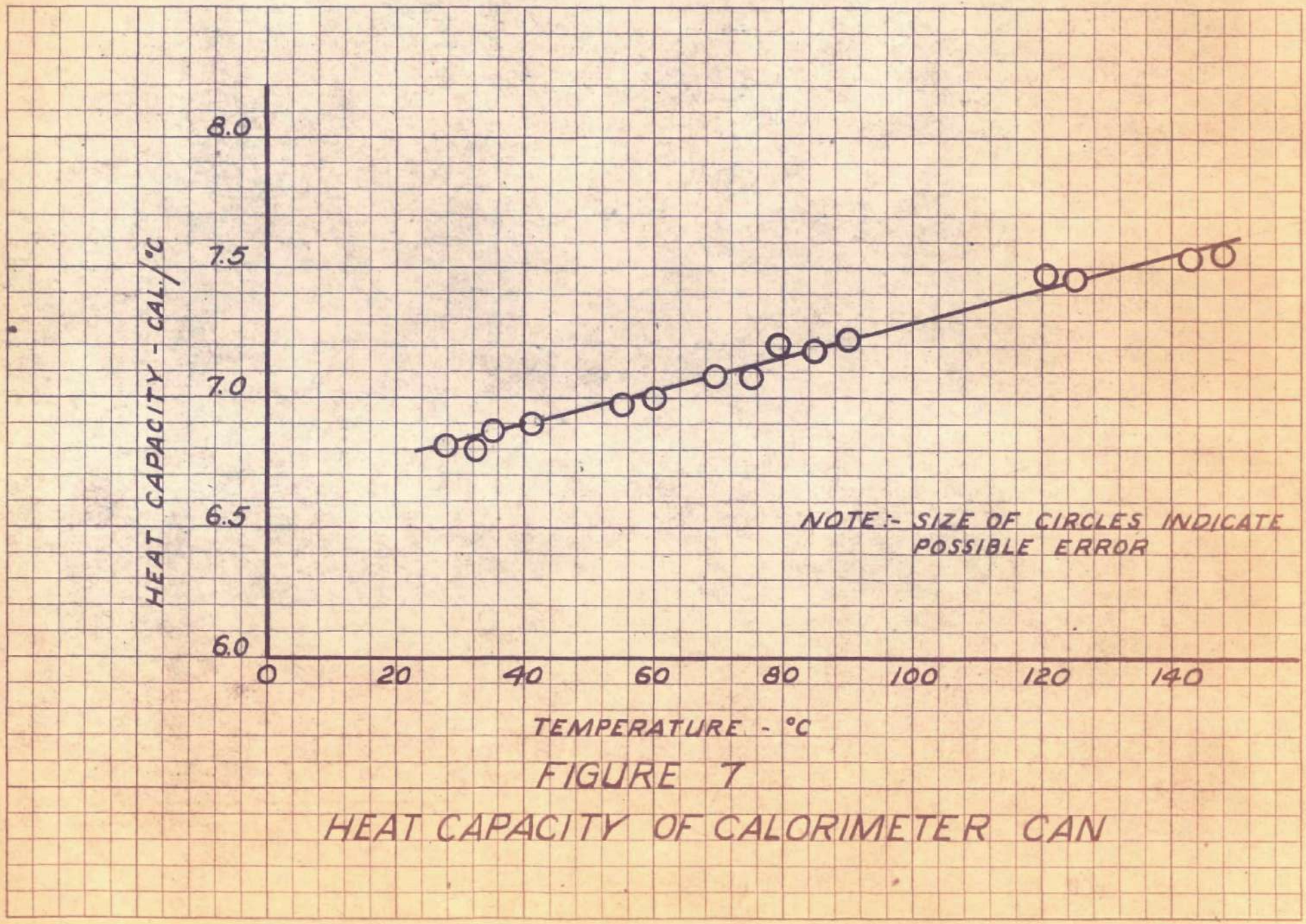

FIGURE 7

HEAT CAPACITY OF CALORIMETER CAN

accuracy expected. With the exception of two of the fifteen determinations, the agreement with values read from the smooth curve is within the calculated accuracy of $\pm 0.65\%$. This is the calibration curve of the empty calorimeter and will be used in subsequent determinations of heat capacity.

The striking feature of the possible errors involved is that the value of the final temperature contributes the largest portion of the possible error. Further refinement in the apparatus must contain measures for reducing this error.

Summarizing the results of calibrating the calorimeter can:

1. The heat capacity of the calorimeter can varies practically linearly between room temperature and 150°C.

2. The heat capacity of the calorimeter can varies from 6.78 cal/°C at 20°C to 7.63 cal/°C at 150°C.

3. The agreement between determinations is about 0.7%.

4. The possible error of the final calorimeter can temperature determines, to a large degree, the accuracy of the heat capacity.

5. The calorimeter responds readily to controls and has a minimum of heat loss.

CHAPTER VIII

THE HEAT CAPACITY OF NAPHTHALENE

Naphthalene was chosen as the first material for measurement of heat capacity because it is easily purified and has been extensively studied by other investigators. The specific heat of naphthalene is not firmly established in the temperature range of this calorimeter, but reliable data do exist from room temperature down to liquid hydrogen temperatures. It was felt that determinations with this calorimeter could be checked to some degree by the published data and thereby give some insight to the absolute accuracy of the calorimeter. Also the data might serve to more firmly establish the heat capacity of naphthalene in the range above room temperature.

The general procedure is the same as that which was described in Chapter VI, with the added manipulation of weighing the sample of naphthalene before charging the calorimeter can.

It was decided that since the naphthalene was relatively large, flaky crystals a more dense loading would be accomplished by melting the naphthalene and then charging the calorimeter can. This procedure entailed some vapor loss that must be estimated. In any case, when the top was soldered on (vacuuum tight) to the calorimeter can, the sample of naphthalene would

melt and some vapor would be lost.

In order to determine this vapor loss, naphthalene was placed in a weighing bottle, weighed and melted. The top was then removed from the bottle and the bottle tilted so that the vapor would be poured out. Then the bottle was left open for ten minutes in order to simulate the calorimeter can containing the molten naphthalene during the soldering operation. (While soldering the top on, the small tube on the top had to be left open so that air as well as some of the vapors could escape through it rather than through the molten solder seal.) The weighing bottle was again weighed and the loss in weight found. An average of three such experiments showed a loss of 0.045 grams $\pm$ 0.02 grams. Accordingly, this correction was taken into account when the calorimeter can was loaded with approximately 21 grams of naphthalene.

It was felt that some change in the amount of solder on the calorimeter can top might occur, thereby adding some uncertainty to the heat capacity of the calorimeter can. Moreover, after the runs were made, inspection of the calorimeter can showed several drops of solder in the bottom. These were deposited during two unsuccessful attempts to charge and seal the can. This factor added some uncertainty to the values found for the specific heat of naphthalene. Two procedures were used to determine the magnitude of this change of heat capacity of the calorimeter can. One method was to

estimate the change in amount of the solder on the can and to calculate the change in heat capacity of the calorimeter can. The second method was to re-determine the heat capacity of the calorimeter can at two or three points. If the change in heat capacity agreed in magnitude by these two methods, then the correction could be applied to the determined values for naphthalene.

The estimated change in heat capacity of the can due to the added solder was 0.13 cal/°C.

Three determinations of the heat capacity of the empty can with the excess solder showed a heat capacity change of 0.19 cal/°C.

These two figures are considered reasonably good checks, and a correction of 0.19 cal/°C was, therefore, added to the heat capacity of the empty can in calculating the specific heat of naphthalene.

The possible errors from all sources are calculated in Appendix F to be about $\pm$ 3%.

The values found for the specific heat of naphthalene are shown in Table VII. Data for the calculation of the specific heat of naphthalene are in Appendix B Table XIII and a sample calculation may be found in Appendix G.

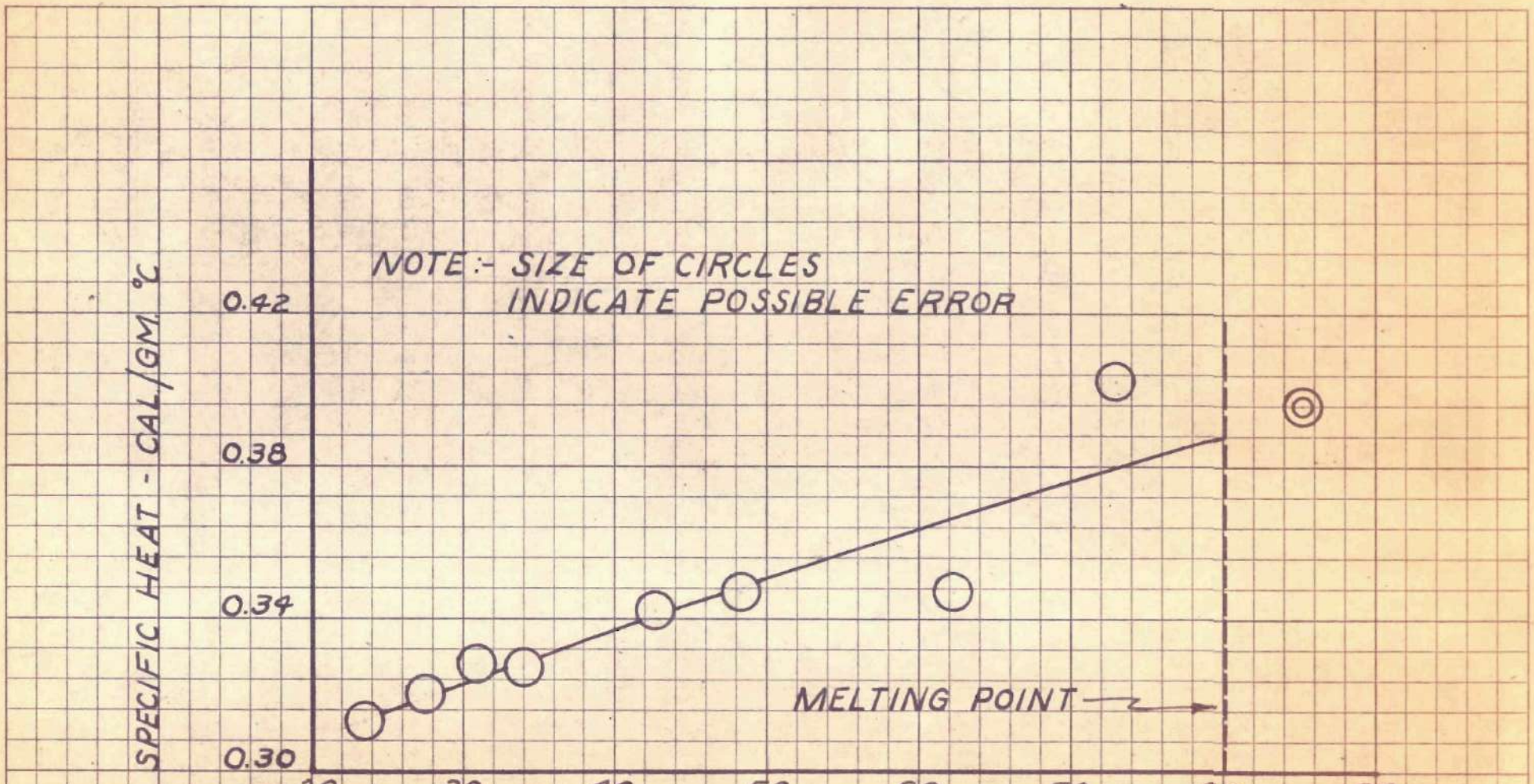

FIGURE 8

SPECIFIC HEAT OF NAPHTHALENE

TABLE VII

THE SPECIFIC HEAT OF NAPHTHALENE

TEMPERATURE °C	STATE	SPECIFIC HEAT in CAL/GM °C
23.5	solid	0.313
27.5	solid	0.320
30.8	solid	0.328
33.9	solid	0.327
42.7	solid	0.342
48.3	solid	0.347
62.4	solid	0.347
73.1	solid	0.402
85.3	liquid	0.396

These data are plotted in Figure 8.

With the exception of two points at the upper temperatures, the agreement between points is within the calculated limits. It is interesting to note that these two determinations were run successively, and when they are taken together as one determination, the point falls on the curve.

A straight line drawn through the plotted points indicated that the change in specific heat is linear in this range.

Figure 9 compares these data with that of Southard (15) and Brickwedde, Huffman, Parks, and Daniels, (16) Andrews,

(15) J. C. Southard and F. G. Brickwedde, J. Am. Chem. Soc., 55, 4378, (1933).

(16) Hugh M. Huffman, Geo. S. Parks, and Albert C. Daniels, J. Am. Chem. Soc., 52, 1547, (1930).

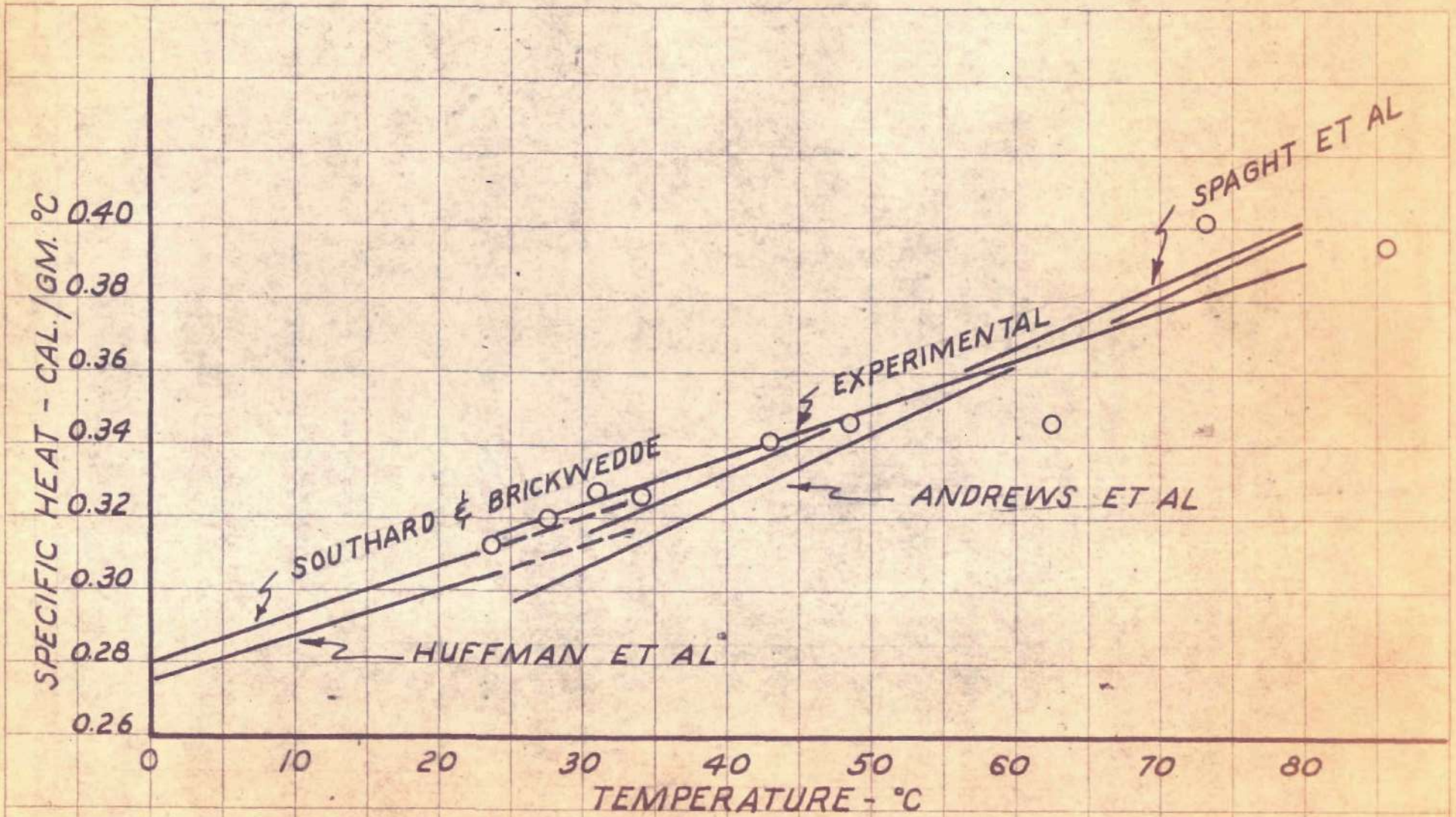

FIGURE 9

COMPARISON OF DATA ON SPECIFIC HEAT OF NAPHTHALENE

Lynn, and Johnston,[17] and Spaght, Thomas, and Parks.[18]

The experimentally determined curve agrees within the experimental limitations of these published data. It is particularly significant that the experimental curve has the same slope and is a continuation of the curve of Southard and Brickwedde. Their data is claimed to be accurate to within 0.1% as compared to 1% to 3% for the other experimentors.

Another significant feature of the experimental curve is that it lies generally higher at the same temperatures than the other curves in the same range.

Appendix B Table XIV and Appendix A Figure 17 show a comparison of the published data on naphthalene .

The heat of melting and the melting point of naphthalene were determined. The procedure was first to find the specific heat of naphthalene about 5°C below the melting point. The sample was heated to the melting point, melted, and heated a few degrees above the melting point. The measured data then permitted the determination of the melting point from a plot of temperature versus time, which shows a constant temperature at the melting point. This point, however, had previously been determined several times during

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(17) D. H. Andrews, Geo. Lynn, and John Johnston, J. Am. Chem. Soc., 48, 1274, (1926).

(18) Monroe E. Spaght, S. Benson Thomas, and Geo. S. Parks, J. Phys. Chem., 36, 882, (1932).

calibration of the calorimeter can thermocouple, so that this run served as a check on the melting point.

The melting temperature then determined and the specific heats before and after melting known, a calculation of the total heat input less the heats required to bring the sample to the melting temperature and from the melting point to the final temperature gave the heat required to melt the sample. Division of this quantity of heat by the sample weight gave the heat required to melt one gram of naphthalene, 34.4 cal/gm. A summary of data taken during the heat of fusion determination is shown in Appendix B Table XV. A sample calculation of the heat of fusion is given in Appendix H.

Values given in the literature give an average value of 35.6 cal/gm [19], which is 3.4% higher than the value found.

From this determination the melting point of naphthalene is found to be 80.12°C as compared to 80.01°C given by Egloff (see footnote 7).

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[19] See Appendix B Table XIV for a tabulation of these values.

CHAPTER IX

CONCLUSIONS

The calorimeter can be used to determine specific heats and heats of transition of solids and liquids in the temperature range from 20°C to 150°C. Lower temperatures may be used by maintaining a colder environment around the outer can.

The absolute accuracy of specific heat measurements made on naphthalene in the range above room temperature was about 3%. This accuracy is limited by the temperature measurement of the sample. Inaccuracies due to heat losses have been minimized and at present constitute only about one-tenth of the total error.

The effective control of the copper adiabatic shield and the aluminum stabilizer shield has made the heat losses small. The aluminum stabilizer shield has greatly increased the ease of control of the adiabatic shield.

The maintenance of low pressure in the environment surrounding the calorimeter can has lessened heat losses due to convection. The vacuum system is excellent in producing and maintaining these low pressures.

The calorimeter can as now constructed is satisfactory for determinations of materials which are not corrosive to copper. The gold plating is not a tight film on the copper

and permits contact between the copper and materials in the can.

Liquids and solids may be used for specific heat measurements. Closely controlled thermal head permits equilibrium to be established even with materials of low heat conductivity.

A good technique is necessary in operating the calorimeter. Vacuum tight solder seals must be made in assembling the calorimeter and the potentiometric measurements and control of heaters require some experience for good manipulation.

This design and construction can be considered successful, but is capable of considerable improvement.

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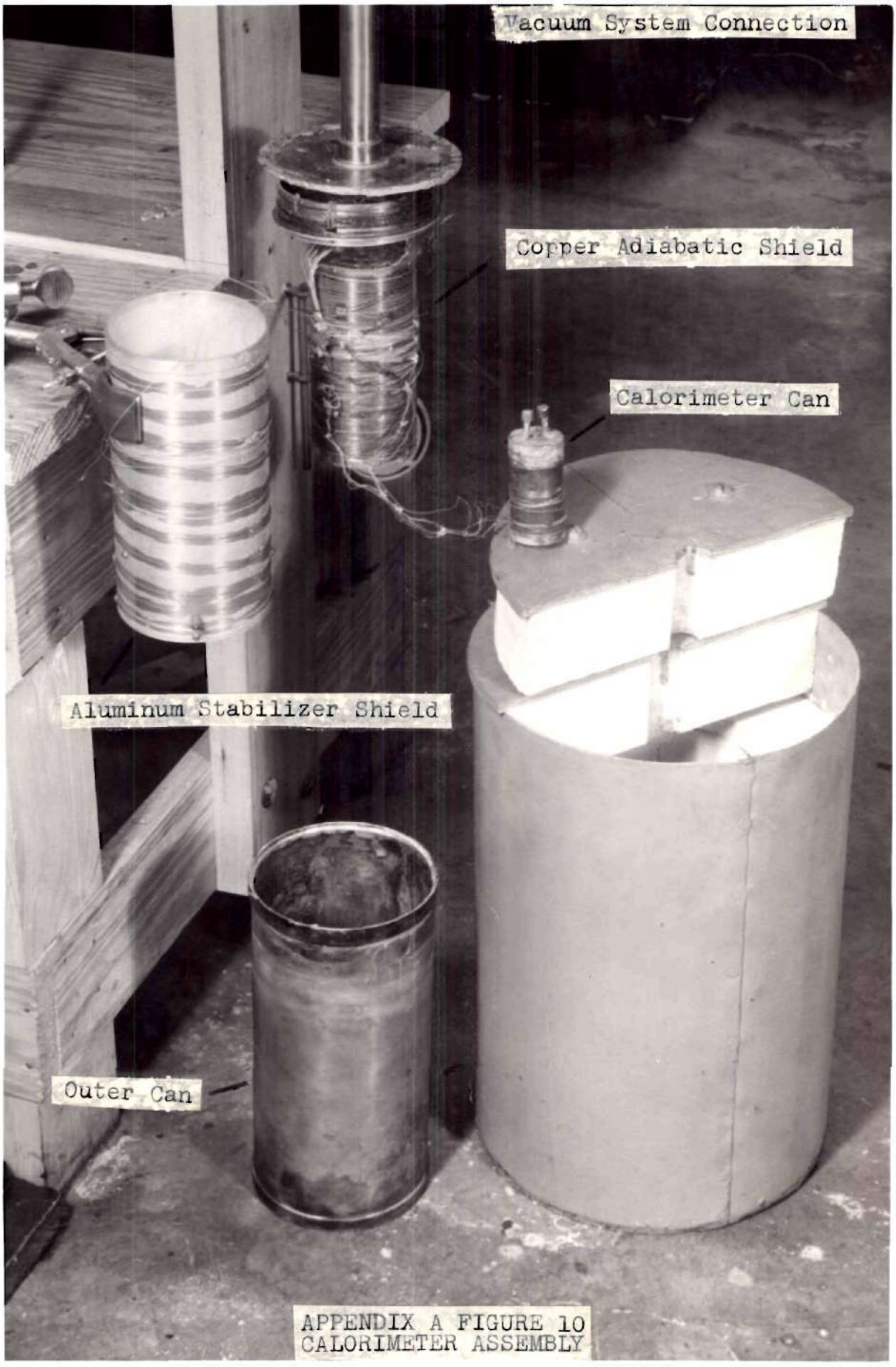
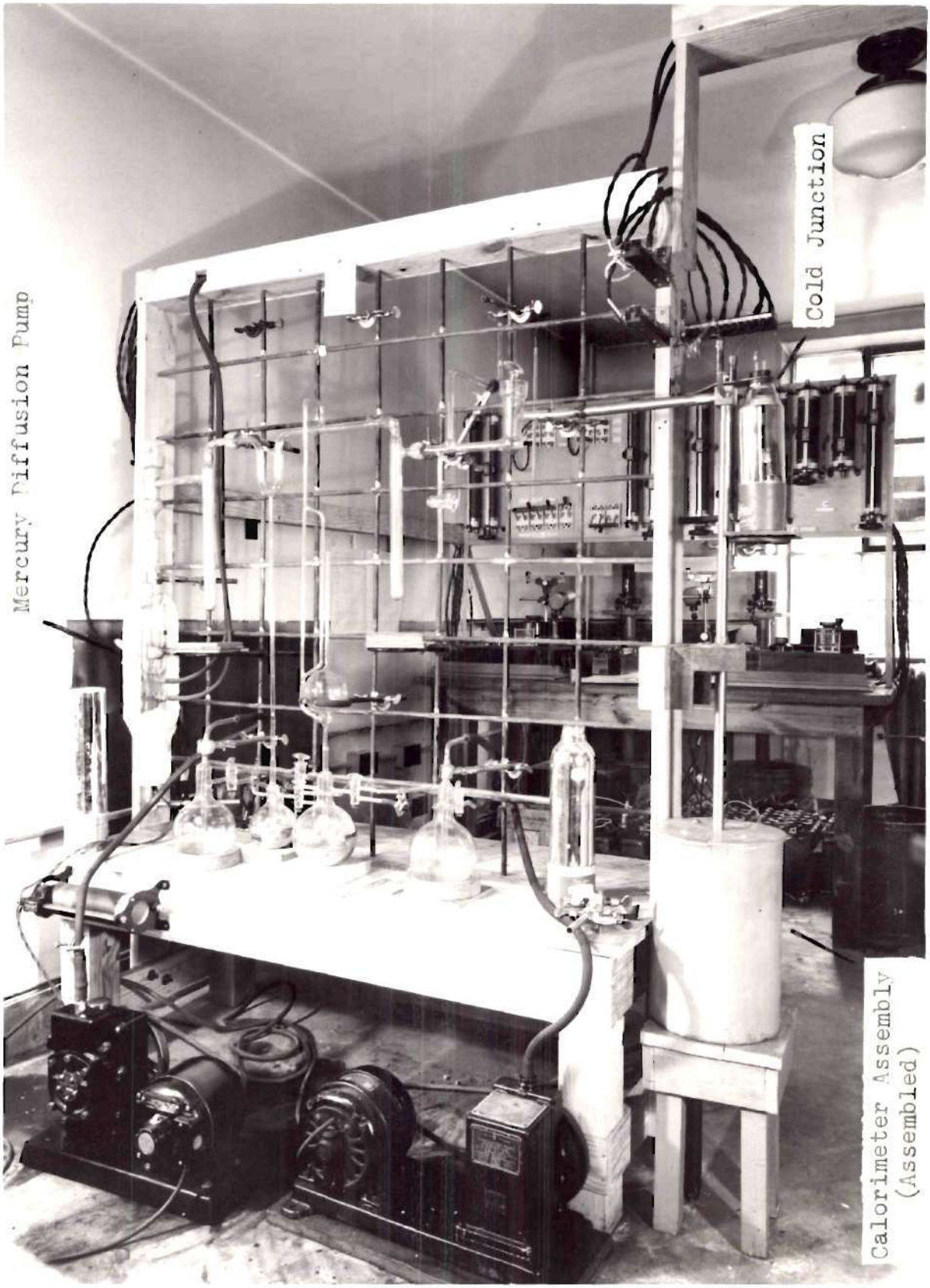
APPENDIX A

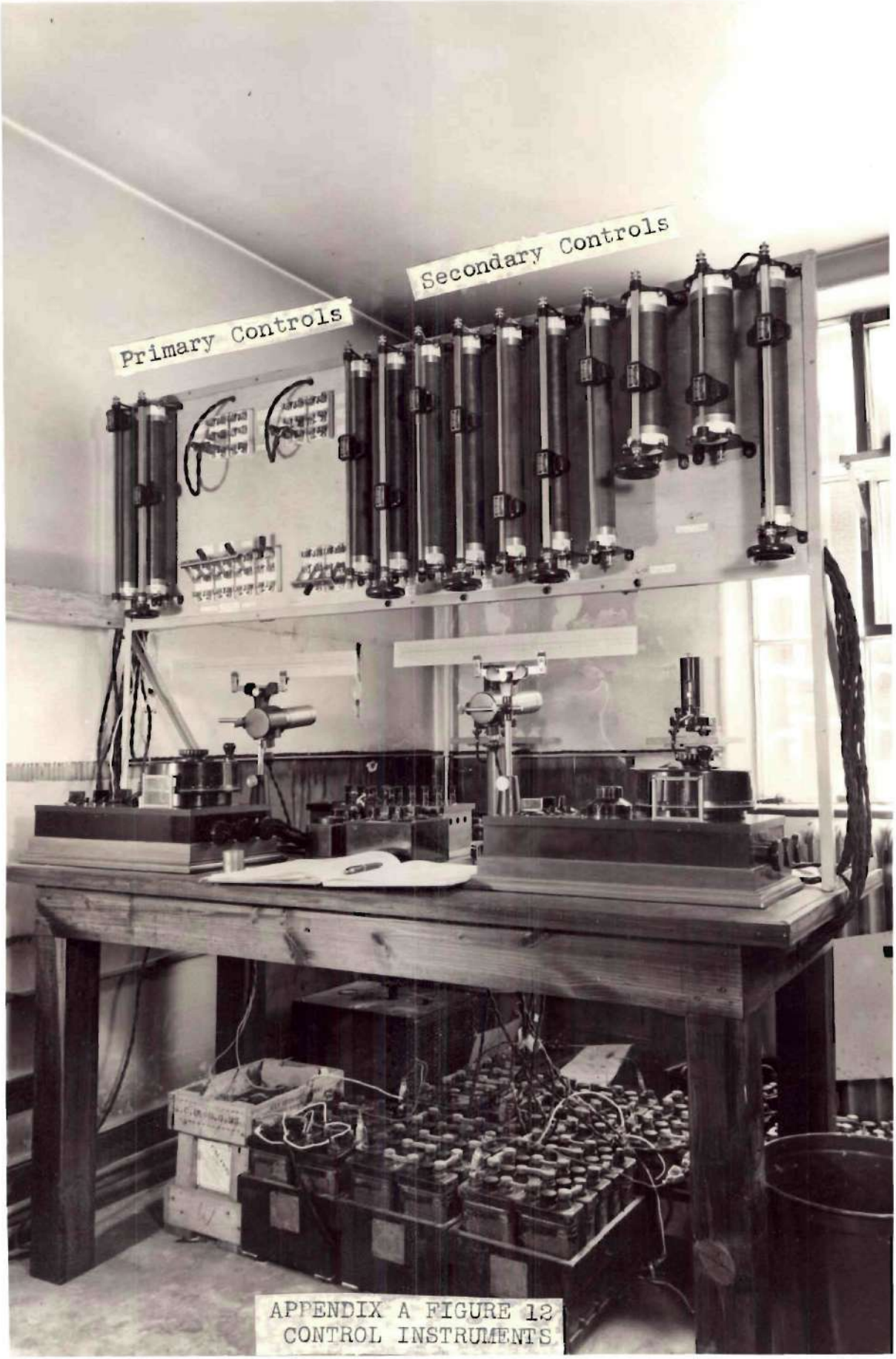
FIGURES



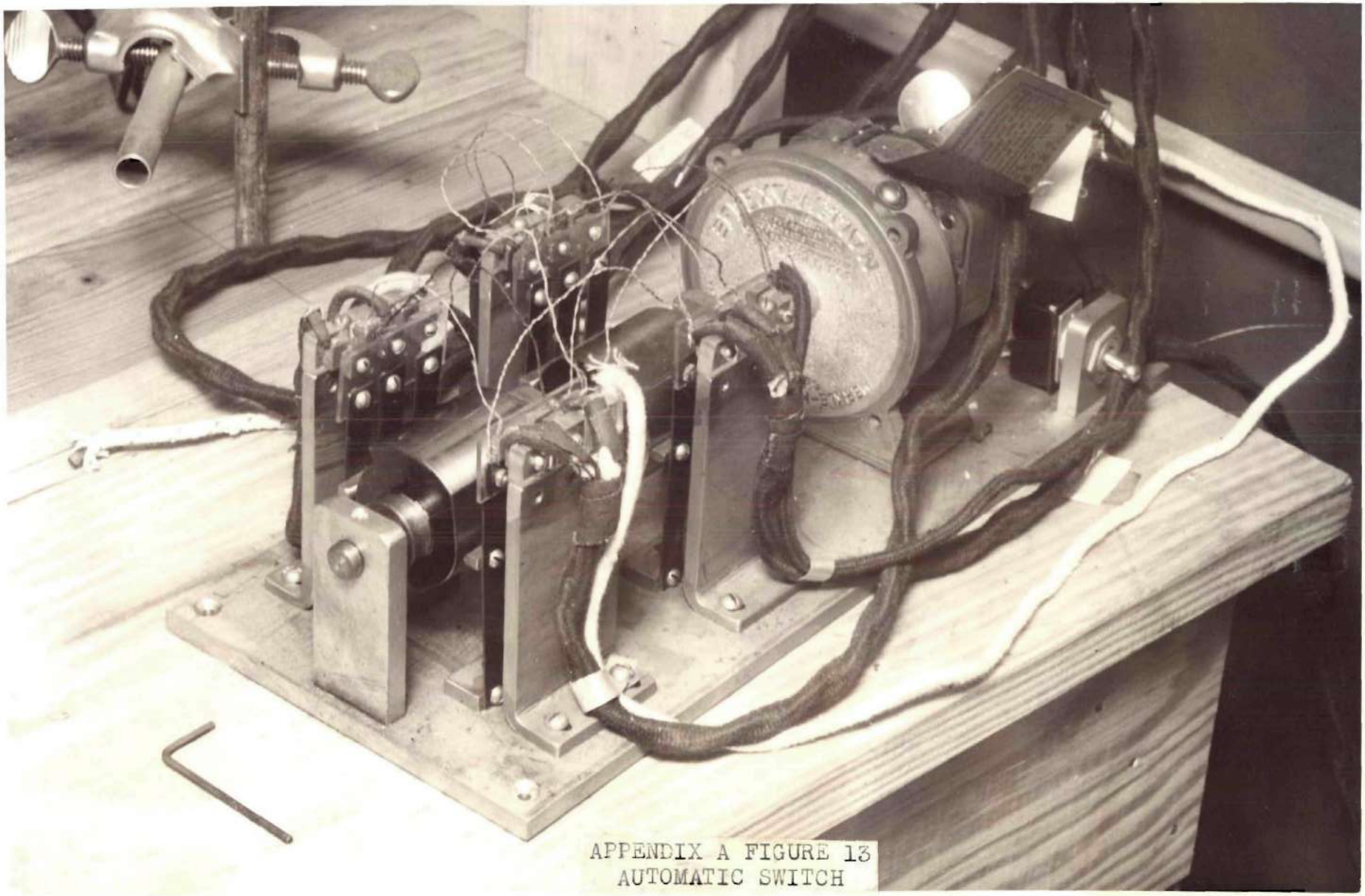
APPENDIX A FIGURE 10
CALORIMETER ASSEMBLY



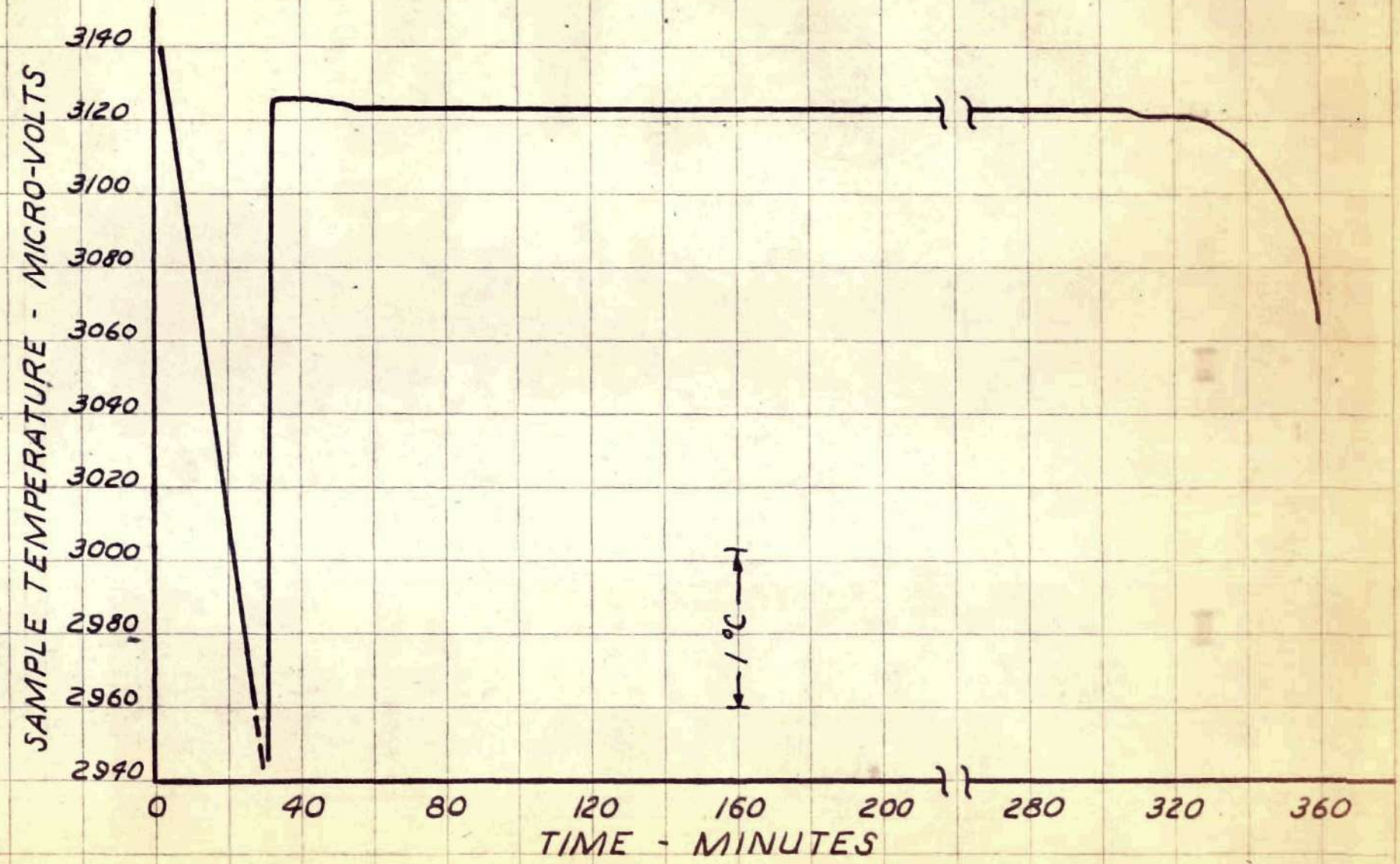
APPENDIX A FIGURE 11
VACUUM SYSTEM



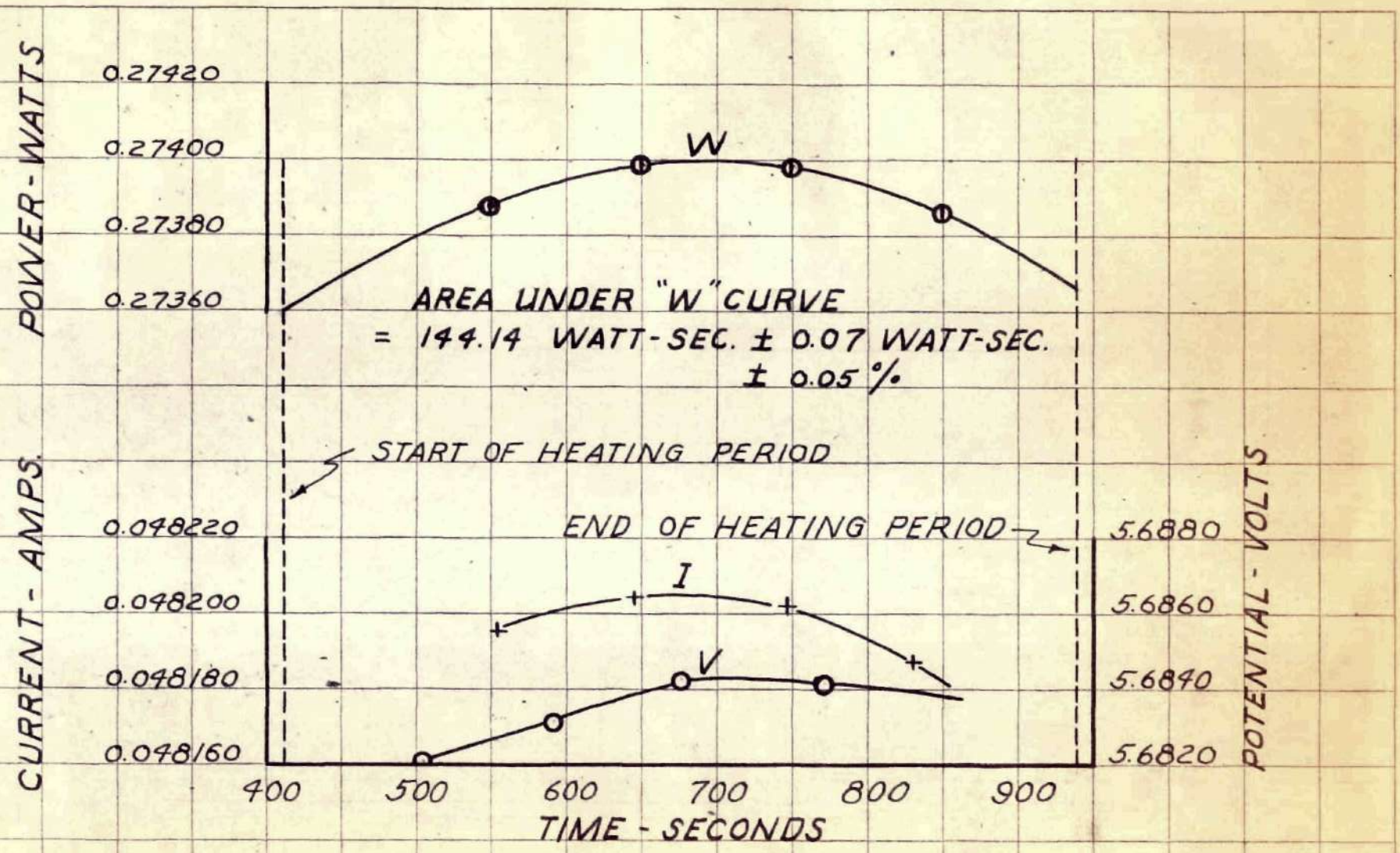
APPENDIX A FIGURE 12
CONTROL INSTRUMENTS



APPENDIX A FIGURE 13
AUTOMATIC SWITCH

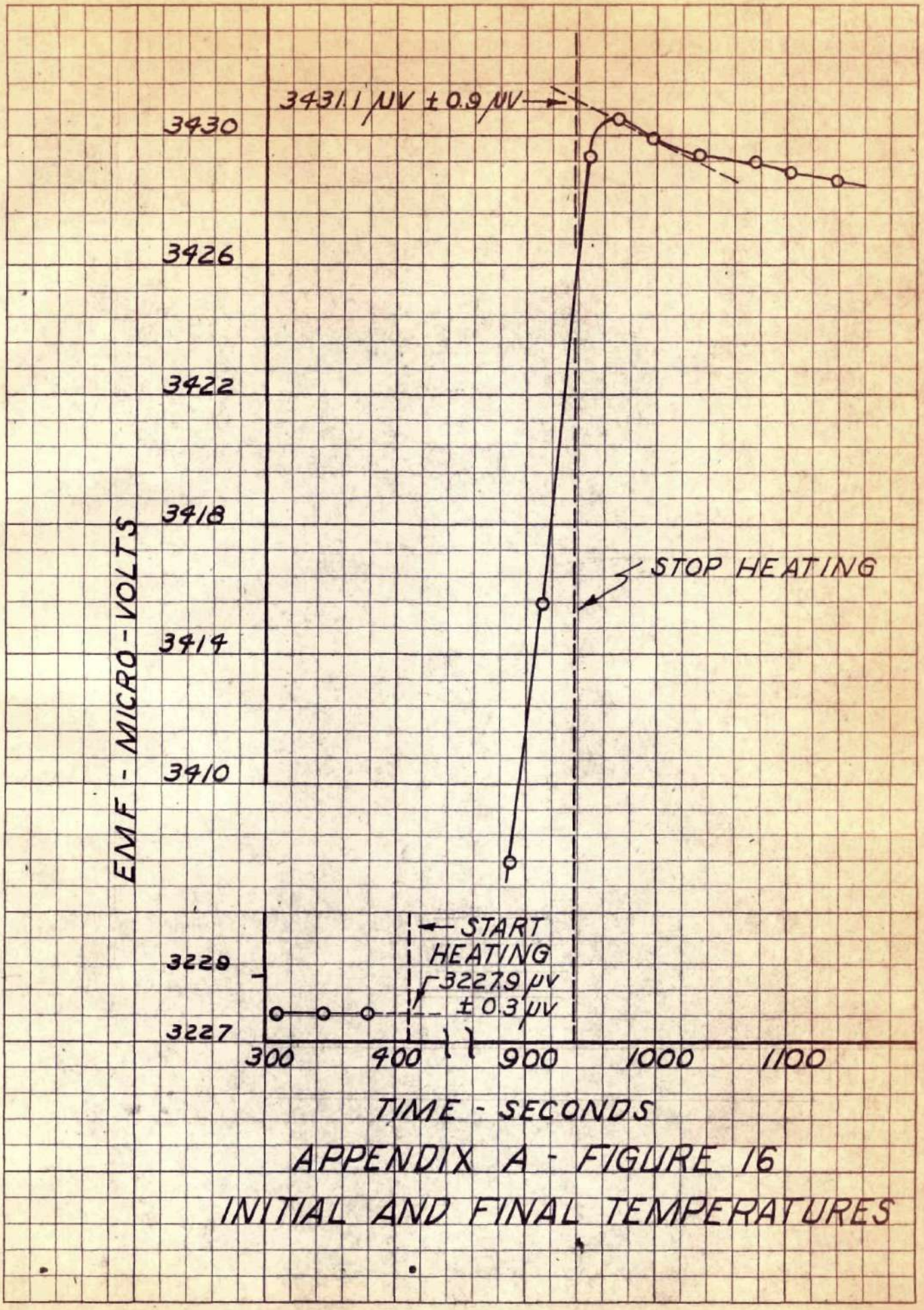


APPENDIX A · FIGURE 14
TYPICAL MELTING CURVE OF NAPHTHALENE



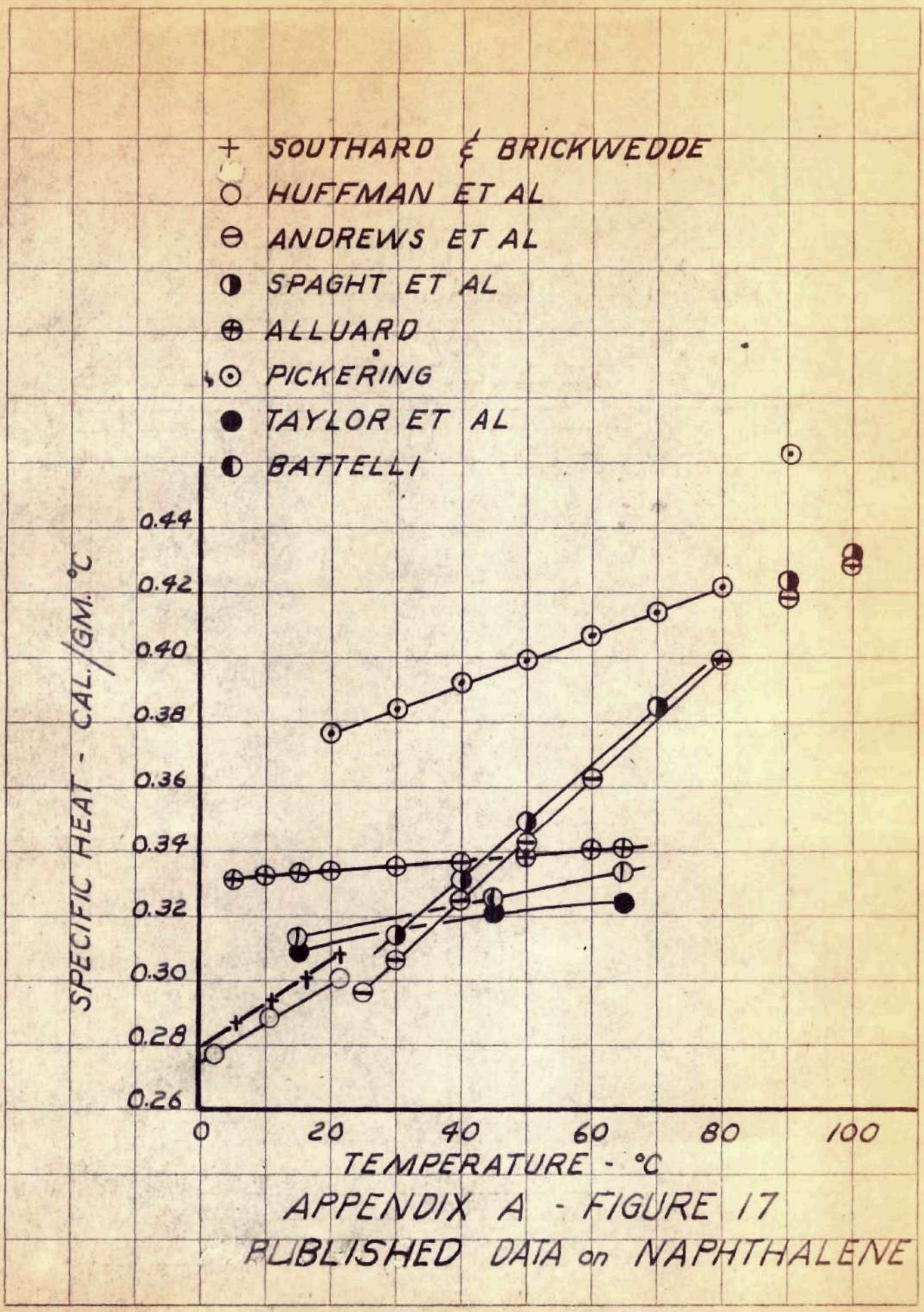
APPENDIX A - FIGURE 15

HEAT INPUT TO CALORIMETER CAN - EMPTY CAN



APPENDIX A - FIGURE 16

INITIAL AND FINAL TEMPERATURES



APPENDIX A - FIGURE 17

PUBLISHED DATA on NAPHTHALENE

APPENDIX B

TABLES

APPENDIX B

TABLE VIII

INSTRUMENTS

PRIMARY CONTROLS:

1. Leeds and Northrup Type K-2 Potentiometer, Serial No. 679633.

2. Leeds and Northrup HS Galvanometer, Serial No. 643993.

   Sensitivity, 0.32 micro-volts/mm.
   Critical Damping Resistance (C.R.D.X.), 50 ohms
   Period, 5.8 seconds
   Resistance, 13.1 ohms

3. Eppley Standard Cell, Serial No. 323979.

4. Leeds and Northrup Volt Box, Serial No. 686172.

5. Lamp (for Galvanometer), Serial No. 679209.

6. Standard Resistance, Serial No. 624178, 10 ohms; and Serial No. 649477, 100 ohms.

SECONDARY CONTROLS:

1. Leeds and Northrup Type K-2 Potentiometer, Serial No. 493180.

2. Leeds and Northrup HS Galvanometer, Serial No. 643992.

   Sensitivity, 0.32 micro-volts/mm.
   Critical Damping Resistance (C.R.D.X.), 49 ohms
   Period, 6 seconds
   Resistance, 12.0 ohms

3. Eppley Standard Cell, Serial No. 233715.

4. Lamp (for Galvanometer), Serial No. 679211.

APPENDIX B

TABLE IX

TEMPERATURE-EMF RELATION FOR COPPER-CONSTANTAN THERMOCOUPLE

$E = 35.68852\ t + 0.04362747\ t^2 - 3.210235 \times 10^{-5}\ t^3$

Reference junction = 0°C 1 μv = 10^{-6} volts

t°C	E-μv	diff.-μv	t°C	E-μv	diff.-μv
1	35.73	35.73	36	1339.83	38.66
2	71.55	35.82	37	1378.58	38.75
3	107.46	35.91	38	1417.40	38.82
4	143.45	35.99	39	1456.31	38.91
5	179.53	36.08	40	1495.29	38.98
6	215.70	36.17	41	1534.35	39.06
7	251.95	36.25	42	1573.50	39.15
8	288.28	36.33	43	1612.72	39.22
9	324.71	36.43	44	1652.02	39.30
10	361.22	36.51	45	1691.40	39.38
11	397.81	36.59	46	1730.86	39.46
12	434.49	36.68	47	1770.40	39.54
13	471.25	36.76	48	1810.02	39.62
14	508.10	36.85	49	1849.71	39.69
15	545.04	36.94	50	1889.48	39.77
16	582.06	37.02	51	1929.33	39.85
17	619.16	37.10	52	1969.26	39.93
18	656.34	37.18	53	2009.26	40.00
19	693.61	37.27	54	2049.34	40.08
20	730.96	37.35	55	2089.50	40.16
21	768.40	37.44	56	2129.74	40.24
22	805.92	37.52	57	2170.05	40.31
23	843.52	37.60	58	2210.43	40.38
24	881.21	37.69	59	2250.90	40.47
25	918.98	37.77	60	2291.44	40.54
26	956.83	37.85	61	2332.05	40.61
27	994.76	37.93	62	2372.74	40.69
28	1032.78	38.02	63	2413.51	40.77
29	1070.88	38.10	64	2454.35	40.84
30	1109.05	38.17	65	2495.26	40.91
31	1147.31	38.26	66	2536.25	40.99
32	1185.66	38.35	67	2577.32	41.07
33	1224.08	38.42	68	2618.46	41.14
34	1262.58	38.50	69	2659.67	41.21
35	1301.17	38.59	70	2700.96	41.29

Appendix B Table IX
(continued)

t°C	E-μv	diff.-μv	t°C	E-μv	diff.-μv
71	2742.32	41.36	116	4676.81	44.48
72	2783.76	41.44	117	4721.36	44.55
73	2825.27	41.51	118	4765.97	44.61
74	2866.85	41.58	119	4810.64	44.67
75	2908.50	41.65	120	4855.38	44.74
76	2950.23	41.73	121	4900.19	44.81
77	2992.03	41.80	122	4945.06	44.87
78	3033.90	41.87	123	4989.99	44.93
79	3075.84	41.94	124	5034.99	45.00
80	3117.86	42.02	125	5080.05	45.06
81	3159.95	42.09	126	5125.17	45.12
82	3202.11	42.16	127	5170.35	45.18
83	3244.34	42.23	128	5215.60	45.25
84	3286.64	42.30	129	5260.91	45.31
85	3329.02	42.38	130	5306.28	45.37
86	3371.46	42.44	131	5351.72	45.44
87	3413.98	42.52	132	5397.22	45.50
88	3456.56	42.58	133	5442.78	45.56
89	3499.22	42.66	134	5488.40	45.62
90	3541.95	42.73	135	5534.08	45.68
91	3584.74	42.79	136	5579.82	45.74
92	3627.61	42.87	137	5625.63	45.81
93	3670.54	42.93	138	5671.49	45.86
94	3713.55	43.01	139	5717.42	45.93
95	3756.62	43.07	140	5763.40	45.98
96	3799.77	43.15	141	5809.45	46.05
97	3842.98	43.21	142	5855.56	46.11
98	3886.26	43.28	143	5901.72	46.16
99	3929.61	43.35	144	5947.95	46.23
100	3973.03	43.42	145	5994.24	46.29
101	4016.51	43.48	146	6040.58	46.34
102	4060.06	43.55	147	6086.98	46.40
103	4103.68	43.62	148	6133.45	46.47
104	4147.37	43.69	149	6179.97	46.52
105	4191.13	43.76	150	6226.55	46.58
106	4234.95	43.82	151	6273.19	46.64
107	4278.84	43.89	152	6319.89	46.70
108	4322.79	43.95	153	6366.64	46.75
109	4366.81	44.02	154	6413.46	46.82
110	4410.90	44.09	155	6460.33	46.87
111	4455.06	44.16	156	6507.25	46.92
112	4499.28	44.22	157	6554.24	46.99
113	4543.56	44.28	158	6601.28	47.04
114	4587.91	44.35	159	6648.38	47.10
115	4632.33	44.42	160	6695.54	47.16

APPENDIX B
TABLE X

Typical Data Sheet for Heat Capacity Determination
Empty Calorimeter Can

Primary Operator

October 20, 1947

Watch No. 1 Min:Sec	Watch No. 2 Min:Sec	Total Time Sec	Cal. Can Thermocouple micro-volts*	Cal. Can Heater Current micro-volts*	Cal. Can Heater Potential micro-volts*	REMARKS
0		0	3224.4			
4:13		253	3228.0			
5:08		308	3227.9			Time=
5:45		345	3227.9			
6:20		380	3227.9			11:51 a.m.
6:51	0	411			START	
	1:33	504			0.56820	
	2:23	554		0.48195		
	3:00	591			0.56832	Vacuum System Pressure is
	3:54	645		0.48204		
	4:30	681			0.56843	1×10^{-4} mm. Hg
	5:10	721		0.48202		
	6:00	771			0.56842	
	7:00	831		0.48187		
	7:56	887	3407.6			
	8:21	912	3415.6			
0	8:46.3	937.3			STOP	Room Temp.=
0:11		948.3	3429.4			23°C
0:33		970.3	3430.5			
1:00		997.3	3429.9			
1:35		1032.3	3429.4			
2:19		1076.3	3429.2			
2:45		1102.3	3428.9			
3:20		1137.3	3428.6			

*Potentiometer Measurement

APPENDIX B

TABLE XI

Typical Data Sheet for Heat Capacity Determination
Empty Calorimeter Can

Secondary Operator

October 20, 1947

Time Hr:Min:Sec	Thermocouple Top Aluminum Shield - μv	DIFFERENCE THERMOCOUPLES			REMARKS
		Top-Body Ad. Shield cm*	Cal. Can-Ad. Sh. cm*	Bottom-Body, Ad. Sh.- cm*	
					Al.Sh.-Ad.Sh.= +0.2 cm*
11:55:30		+1.7	+1.2	+0.25	
11:57:00			+0.7		Heat on Can
11:57:05			-0.5		
11:57:15			+0.9		
11:57:35	3264.6		+0.7		
11:59:00			+0.5		
12:00:00			0		
12:00:30			-0.35		
12:01:00			-0.4		
12:01:15		+2.4	-0.3	-3.2	
12:02:00		+2.0	+0.2	-2.4	
12:04:00		+2.4	-1.3	-3.3	
12:05:00			-0.6		
12:05:30			-0.6		
12:06:30			-0.5		
12:06:40					Heat off Can
12:06:50			+1.5		
12:07:00			+0.7		
12:07:15			-0.5		
12:07:30			+0.4		
12:08:00		+2.2	+0.15	-1.1	
12:09:00			+0.35		
12:10:30	3304.5		+0.35		

*Galvanometer Scale Deflection, 1 cm = 0.025°C approximately

APPENDIX B

TABLE XII

Heat Capacity of Calorimeter Can

Run #	Cal/°C	°C
1	6.80	32.24
4	6.810	27.95
5	6.873	35.15
6	6.896	40.81
7	6.973	55.01
8	6.996	59.86
9	7.093	69.40
10	7.077	74.80
11	7.208	79.71
12	7.187	85.01
13	7.221	89.99
14	7.479	120.38
15	7.459	124.82
16	7.504	143.29
17	7.554	148.07

APPENDIX B TABLE XIII

DATA FOR SPECIFIC HEAT OF NAPHTHALENE (20)

emf $-\mu v$		Temp. - °C		Δt	Heat Input	Heating Interval $\Delta\theta$	C_p (n+can)	C_p(can)	S-cal/gm °C
start	end	start	end	°C	W-Watts	Sec.	$\frac{w\ \Delta\theta}{4.186\ \Delta t}$	cal/°C	$\frac{C_p(n+can) - C_p(can)}{W}$
768.0	959.3	20.989	26.065	5.076	0.49459	592.4	13.79	6.99	0.313
946.3	1081.3	25.722	29.273	3.551	0.21017	988.4	13.97	7.02	0.320
1025.4	1255.9	27.806	33.826	6.020	0.49336	723.7	14.17	7.04	0.328
1205.8	1312.9	32.524	35.303	2.779	0.27502	598.9	14.16	7.05	0.327
1488.5	1715.3	39.826	45.606	5.780	0.49150	716.2	14.55	7.11	0.342
1724.0	1919.2	45.826	50.746	4.920	0.49072	616.4	14.69	7.14	0.347
2268.8	2508.5	59.442	65.323	5.881	0.53337	681.8	14.77	7.23	0.347
2732.1	2927.1	70.753	75.446	4.693	0.53163	591.5	16.01	7.28	0.402
3233.0	3449.6	82.731	87.837	5.106	0.60723	564.0	16.02	7.41	0.396

(20) See Appendix F for sample calculation of possible error.

APPENDIX B TABLE XIV

PUBLISHED DATA ON NAPHTHALENE

SPECIFIC HEAT - CAL/gm. °C

°C	Southard (15) and Brickwedde	Huffman (16) et al	Andrews (17) et al	Spaght (18) et al	Alluard (21)	Taylor (22) et al	Battelli (23)	Pickering (24)
-21.2		0.254						
0.05	0.2800							
2.3		0.278						
5					0.3323			
5.53	0.2871							
10					0.3330			
10.5		0.289						
10.93	0.2941							
15					0.338	0.309	0.314	
16.26	0.3010							
20					0.3345			0.3764
21.52	0.3088							
21.9		0.305						
25			0.2973					
30			0.3067	0.315	0.3360			0.3840
40			0.3254	0.332	0.3375			0.3916
45						0.321	0.326	
50			0.3437	0.350	0.3390			0.3992
60			0.3629	0.367	0.3405			0.4068
65					0.3413	0.324	0.334	
70			0.3816	0.385				0.4144
80			0.4004					0.4220
90			0.4193	0.424				
90.5								0.4824
100			0.4284	0.432				
Accuracy	± 0.1%	>1%	± 3%					
Heat of Fusion- Cal/gm			35.45	35.8	35.679			35.625
Accuracy			± 1%	± 3%				

(15) J. C. Southard and F. G. Brickwedde, J. Am. Chem. Soc., 55, 4378 (1933).

(16) H. M. Huffman, G. S. Parks, and A. C. Daniels, J. Am. Chem. Soc., 52, 1547 (1930).

(17) D. H. Andrews, Geo. Lynn, and John Johnston, J. Am. Chem. Soc., 48, 1274 (1926)

(18) M. E. Spaght, S. B. Thomas, and G. S. Parks, J. Phys. Chem., 36, 882-8 (1932).

(21) Alluard, Ann. Chim. Phys. (3) 57, 438 (1859)

(22) C. A. Taylor and W. H. Rinkenback, J. Am. Chem. Soc., 46 1504 (1924).

(23) Battelli, Atti ist. Veneto (6) 3 disp. 10, 1781 (1884-1885).

(24) S. U. Pickering, Proc. Royal Soc. of London, 49 11 (1891).

APPENDIX B TABLE XV

SUMMARY OF HEAT OF FUSION DATA

October 29, 1947

Calorimeter Can Contains 21.74 gms. of Naphthalene.
Pressure in Vacuum System = 10^{-3} mm.

Time Min.	Temp. of Sample °C	Heating Rate Cal/min.	Difference Thermocouples Top-Body Ad. Sh. °C	Cal.Can-Ad. Sh. °C	Bottom-Body Ad. Sh. °C	REMARKS
0	74.940					
1.58	74.947					
2.58	74.947		+0.03	-0.03	+0.06	
2.67	-	start				
4.98	75.957	8.715	+0.03	-0.01	-0.10	
23.00	79.871	8.724	+0.04	-0.04	-0.03	
35.78	80.074	8.721		-0.005	-0.03	
41.95	80.120	8.720	+0.01	-0.005	-0.04	
49.87	80.126	8.719	+0.01	0.00	-0.03	Vacuum System Pressure = 10^{-3} mm.
69.53	80.285	8.716		+0.04		Temp. Top Al. Shield = 80.1°C
85.37	80.361	8.702		-0.01		
98.62	80.943	8.720	-0.02	-0.01	-0.06	Temp. Top Al. Shield = 78.8°C
102.32	82.379	8.717		-0.008		
102.67	-	stop		-0.005		
103.53	82.720			-0.10		
106.92	82.760		-0.03	+0.005	-0.07	
110.42	82.760			-0.005		Temp. Top Al. Shield = 79.9°C

APPENDIXES C, D, E, F, G, AND H

Sample Calculations

APPENDIX C

Effect of Thermal Heads on Calorimeter Can

The procedure used was to adjust the adiabatic shield to a constant temperature difference between it and the calorimeter can. Then the calorimeter can temperature was read every minute for several minutes. The calorimeter can temperature was then plotted against time and the slope of the resulting line determined. This slope gave the change of calorimeter can temperature, t, with respect to time, e, dt/de. This may be translated to actual heat loss in calories with respect to time by multiplying by the heat capacity of the can in cal/°C.

If the slope of the line, dt/de, is 0.015°C/min and the heat capacity of the can is taken to be 7 cal/°C (an average value), then

$$dq/de = 0.015°C/min \times 7\ cal/°C$$
$$= 0.105\ cal/min.$$

When the time during which a given temperature difference between the calorimeter can and adiabatic shield exists is known, the loss or gain of heat by the calorimeter can may be determined.

If the adiabatic shield was hotter than the calorimeter

can by 0.33°C for 30 seconds,

$$\Delta q = 0.105 \text{ cal/min} \times 0.5 \text{ min} = 0.053 \text{ cal}$$

The calorimeter can then gained 0.053 calories from the adiabatic shield.

APPENDIX D

Calculation of Heat Capacity

Temperature Change:

Initial Temperature = 3227.9 micro-volts
(from Appendix A Figure 16)

Final Temperature = 3431.1 micro-volts
(from Appendix A Figure 16)

From Appendix B Table IX:

82°C = 3202.11 micro-volts
83°C = 3244.34 micro-volts
87°C = 3413.98 micro-volts
88°C = 3456.56 micro-volts

$$\text{Initial Temperature} = \frac{3227.9 - 3202.11}{3244.34 - 3202.11} + 82 = 82.611°C$$

$$\text{Final Temperature} = \frac{3431.1 - 3413.98}{3456.56 - 3413.98} + 87 = 87.402°C$$

$$\text{Average Temperature} = \frac{82.611 + 87.402}{2} = 85.01°C$$

Temperature Change = 87.402° - 82.611° = 4.791°C

Heat Input to Calorimeter Can Heater:

$$\frac{144.14 \text{ watt-sec}}{4.18608 \text{ watt-sec/cal}} \text{ (from Appendix A Figure 15)} = 34.433 \text{ cal.}$$

$$\text{Heat Capacity} = \frac{34.433 \text{ cal}}{4.791°C} = 7.19 \text{ cal/°C at } 85.01°C$$

APPENDIX E

Calculation of Possible Error in Heat Capacity

1. Temperature Rise: (See Figure 16 Appendix A)

Final Temperature	= 3431.1 micro-volts	$\pm$ 0.9 micro-volts
Initial Temperature	= 3227.9 micro-volts	$\pm$ 0.3 micro-volts
Temperature Rise	= 203.2 micro-volts	$\pm$ 1.2 micro-volts
		$\pm$ 0.55%

2. Heat Input: (See Figure 15 Appendix A)

144.14 watt-sec $\pm$ 0.07 watt-sec
$\pm$ 0.05%

3. Heat Loss: An average rate of heat loss is taken as 0.05 cal/min from drift rate measurements. (See Appendix C)

The time during which this rate obtained is taken to be 20 seconds.

Then:

$$0.05 \text{ cal/min} \times \frac{20}{60} \text{ min} = 0.017 \text{ cal}$$

$$\frac{0.017}{34.4 \text{ (heat input)}} = 0.05\%$$

This uncertainty in heat loss is believed to be the maximum under normal operating conditions.

4. Total:

$$0.55\% + 0.05\% + 0.05\% = 0.65\%$$

APPENDIX F

Possible Error In Heat Capacity Of Naphthalene

1. Weight of Naphthalene, W:

Weight in Air	=	21.7888 gms.	± 0.0002 gms.
Weight in Vacuo	=	21.7854 gms.	± 0.0004 gms.
Vapor loss Correction	=	0.045 gms.	± 0.02 gms.
Weight of Sample	=	21.740 gms	± 0.02 gms.
			± 0.092%

2. Temperature Rise:[25]

$$\frac{1.2 \text{ micro-volts}}{203.2 \text{ micro-volts}} = \pm 0.55\%$$

3. Heat Input:

$$\frac{0.07 \text{ watt-sec}}{144.14 \text{ watt-sec}} = \pm 0.05\%$$

4. Heat Loss:[25]

± 0.05%

5. Heat Capacity of Calorimeter Can, C_p (can):

From Curve (Figure 7)	=	7.00 cal/°C	± 0.045 cal/°C
Correction (Excess Solder)	=	0.19 cal/°C	± 0.060 cal/°C
C_p(can)	=	7.19 cal/°C	± 0.105 cal/°C
			± 1.46%

---

(25) See Appendix E for detailed calculation.

6. Heat Capacity of Naphthalene, $C_p(N)$:

$$C_p(N) = \frac{C_p\ (N + Can) - C_p\ (Can)}{W}$$

Possible Error in $C_p(Can) = \pm 0.105$ cal/°C

Possible Error in $C_p(N + Can) =$

$$(0.55\% + 0.05\% + 0.05\%)\ 14^{(26)} = \pm 0.091 \text{ cal/°C}$$

Possible Error in $C_p(N + Can) - C_p(Can) =$

$$0.105 + 0.091 = 0.196$$

$$\frac{0.196}{7^{(27)}} = 2.8\%$$

Possible Error in $C_p(N) =$

$$2.8\% + 0.092\% = 2.892\% = 2.9\%$$

---

(26) Average value from Appendix B Table XIII.

(27) Average value of $C_p(N)$ in cal/°C from Appendix B Table XIII.

APPENDIX G

Sample Calculation Of Heat Capacity Of Naphthalene

Temperature Change, Δt:

initial, t_1' = 768.0 micro-volts
final, t_2' = 959.3 micro-volts

from Appendix B Table IX:

20°C = 730.96
21°C = 768.40
26°C = 956.83
27°C = 994.76

$$t_1 = \frac{768.0 - 730.96}{768.40 - 730.96} + 20 = 20.989°C$$

$$t_2 = \frac{959.3 - 956.83}{994.76 - 956.83} + 26 = 26.065°C$$

$$\Delta t = 26.065 - 20.989 = 5.076°C$$

$$\text{Average } t = \frac{26.065 + 20.989}{2} = 23.53°C$$

Heat Input, W ($\Delta\theta$):

W = 0.49459 watts, $\Delta\theta$ = 592.4 sec.

$$\frac{W\Delta\theta}{4.186} = \frac{0.49459 \times 592.4}{4.186} = 69.99 \text{ cal.}$$

Heat Capacity of Naphthalene + Can:

$$\frac{W\Delta\theta}{4.186\,\Delta t} = \frac{69.99}{5.076} = 13.79 \text{ cal/°C at } 23.5°C$$

Heat Capacity Of Calorimeter Can:

C_p (from Figure 7) = 6.80 cal/°C at 23.5°C

Correction = +0.19 cal/°C (from page 73)

C_p = 6.80 + 0.19 = 6.99 cal/°C

Specific Heat Of Naphthalene:

Weight in vacuo, of naphthalene, W, = 21.740 gms.

$$S = \frac{C_p(N + Can) - C_p(Can)}{W} = \frac{13.79 - 6.99}{21.740} =$$

0.313 cal/gm °C at 23.5°C

APPENDIX H

Sample Calculation Of Heat Of Fusion

1. Initial Temperature (From a plot similar to Appendix A Figure 16)

$$\frac{2906.3 - 2866.85}{41.65} + 74 = 74.947°C$$

2. Melting Point (From a plot similar to Appendix A Figure 14)

$$\frac{3122.9 - 3117.86}{42.09} + 80 = 80.120°C$$

3. Final Temperature (From a plot similar to Appendix A Figure 16)

$$\frac{3234.2 - 3202.11}{42.23} + 82 = 82.760°C$$

4. Average Temperature Of Solid Naphthalene

$$\frac{80.120 + 74.947}{2} = 77.5°C$$

5. Average Temperature of Liquid Naphthalene

$$\frac{82.760 + 80.120}{2} = 81.4°C$$

6. Total Heat Input (From a plot similar to Appendix A Figure 15)

$$\frac{3642 \text{ watt-sec}}{4.186 \frac{\text{watt-sec}}{\text{cal}}} = 870.1 \text{ cal.}$$

Appendix H (continued)

7. Heat Capacity Of Calorimeter Can + Naphthalene
Sample Weight = 21.74 gms.

Average Temp. °C	Naphthalene		Calorimeter Can		Total
	cal/gm °C (Figure 8)	cal/°C	cal/°C (Figure 7)	Correction (page 73)	cal/°C
77.5	0.387	8.41	7.14	0.19	15.74
81.4	0.392	8.52	7.16	0.19	15.87

8. Heat Required To Heat To Melting Point

$15.74\ (80.120 - 74.947) = 81.42$ cal

9. Heat Required to Heat From Melting Point To Final Temperature

$15.87\ \ (82.760 - 80.120) = 41.89$ cal

10. Heat Required to Melt Naphthalene

$870.1 - 81.42 - 41.89 = 746.8$ cal

11. Heat Of Fusion

$$\frac{746.8}{21.74} = 34.4 \text{ cal/gm}$$